Appendix A

Calibrations and Logistics for Field Sampling

The six hi-volume samplers were recalibrated at AIHL using the orifice plate technique. Immediately following this, the samplers were evaluated for equivalency by sampling for seven $2^{\rm H}$ -hour periods and determining total suspended particulate (TSP). Figure A-1 shows the positioning of the samplers for this work. Sampler locations were altered, as shown, to minimize bias due to locations. The results of this study are given in Table A-1. For the seven sampling days the mean coefficient of variation between the six samplers was 4.8% with a mean TSP of $3^{\rm H}$ $\mu\rm{g/m}^3$. The results for the six hi-vol samplers were judged sufficiently equal to permit reliable field sampling.

A problem was experienced with the flow meter in Instrument No. 4 at Riverside used for 2-hour samples. Flow readings on this instrument were approximately 30 units compared to 50 at Berkeley. Table A-2 summarizes the behavior of all instruments used. Results from Instrument 4, a 2-hour sampler, were clearly anomalous if values around 30 are assumed to be correct. The resulting apparent 14-hour TSP measurements were approximately three times those from the 14-hour sampler adjacent to it. However, the actual weight of material on the 2-hour filters from hi-vol No. 4 was similar to those at other sites sampling at the same time, suggesting the instrument really was sampling close to same flow as in Berkeley.

Two assumptions were tested to serve as the basis for correcting the flow data from hi-vol No. 4:

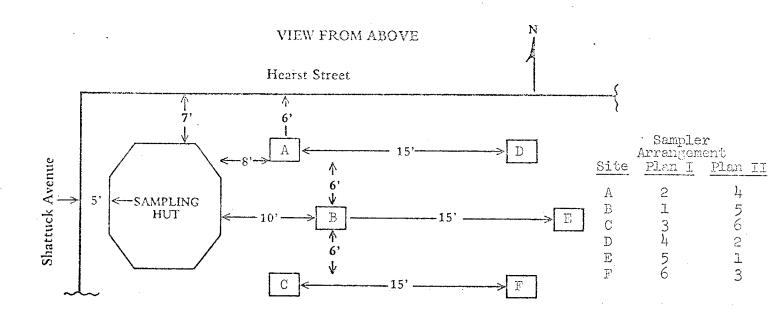
Assumption A: Assume hi-vol No. 4 behaves like units 1, 6, 2, and 5. Then No. 4 should have read about 4 units higher than in Berkeley.

Assumption B: Assume hi-vol No. 4 behaves like No. 3. Then No. 4 should have read about 10 units higher than in Berkeley.

Using Assumptions A and B, flows were calculated and the resulting 14-hour concentration calculated from seven 2-hour filters and compared to those observed.

<u>Site</u>	14-hour obs/14-hour cale TSP
Pasadena Pomona Riverside - Assumption A Riverside - Assumption B	0.72 0.77 0.66 0.78

Since it is plausible that artifact SO₄ causes some of the discrepancy between calculated and observed TSP and that such effects should be lower in Riverside because of lower SO₂, we conclude that Assumption B is more nearly correct. All concentrations from samples obtained on Instrument No. 4 were calculated accordingly, but their absolute values must be considered less reliable than those from the other samples.



VIEW FROM SIDE LOOKING SOUTH

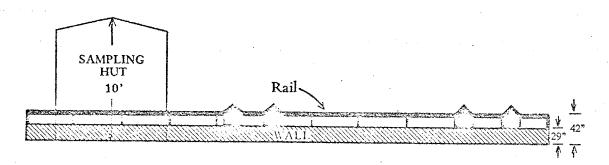


Figure A-1. Arrangement of High Volume Air Samplers on Roof of the State Health Department.

SOURCE: STATE OF CALIFORNIA DEPARTMENT OF HEALTH AIR AND INDUSTRIAL HYGIENE LABORATORY, BERKELEY

Table A-1

OBSERVED VALUES OF TOTAL SUSPENDED PARTICULATE IN 24-HOUR SAMPLING $(\mu g/m^3)$

	C. V. thi? (%)	9.4	8°	7.4	5.8	3.6	7.1	9.4
	Mean	29.5 ± 1.4	48.3 ± 1.6	29.4 + 1.4	25.9 ± 1.5	27.1 ± 1.0	48.8 + 3.4	31.5 ± 1.4
•	9	28.98	48.37	27.94	23.4	27.7	51.8	☆ !
	5	30.59	49.93	29.40	27.1	28.5	52.7	31.44
	4	90.46	49.19	29.13	56.9	26.4	9.44	32.07
	† co	27.75	45.48	28.12	54.6	25.7	44.8	29.19
	2	30.90	92.74	30.29	26.5 26.7 24.6	27.1	9.64	31.57
	1	28.07	49.20	31.61	26.5	27.1	9.64	33.12
	Trial	Ч	CI	က	7†	<u>τ</u>	9	2
	Plan	Н	Н	Н	Ħ	II	II	н

Sampler 6 not admissable for comparison for this trial due to timer problems.

 $^{^{}k\!n\!k}$ Coefficient of variation.

Table A-2

COMPARISON OF HI-VOL FLOW METER READINGS IN BERKELEY AND AT FIELD SITE

Inst. No.	Ave. Flow Berkeley	Reading ^a <u>Field</u>	Δ Flow	Field Location
1	48.5	53.25	+ 4.75	Pasadena
6	40.0	44.5	+ 4.50	Pasadena
2	47.5	51.5	+ 4.00	Pomona
5	37.0	41.0	+ 4.00	Pomona
3	46.0	56.5	+10.5	Riverside
14	48.0	30.0	-18.0	Riverside

a. Average of initial and final flow readings.

The DASIBI analyzers at Pasadena and Pomona were calibrated according to ARB's UV procedure. At Riverside, the REM chemiluminescent ozone analyzer was calibrated against 2% neutral buffered KI at the request of the Riverside staff. The resulting 0_3 values are approximately 22% higher than values expected by the ARB UV procedure.* Accordingly, all 0_3 values from Riverside were multiplied by 0.78.

Filters were packaged in aluminum foil lined manila folders to minimize carbon contamination. These, in turn, were inserted in manila envelopes. Immediately vollowing sampling, loaded filters, packaged as described, were placed in closed polyethylene bags and immediately frozen. Samples were subsequently transferred to a cold room maintained at $\leq 5^{\circ}$ C until completion of the study. Samples were transported to AIHL over dry ice and stored at -10° C until ready for analysis.

A set of instructions for sampler operators is included at the end of this Appendix.

^{*}D. Grosjean, private communication.

INSTRUCTIONS FOR FIELD PERSONNEL

Carbonaceous Material Characterization Study

- 1. Sampling is being conducted at three locations:
 - a. Cal Tech on roof of Keck Lab., Pasadena
 - b. Roof of Pomona station of LAAPCD, 924 North Garey, Pomona
 - c. Top of ARB trailer adjacent to the Fawcett Lab., U.C. Riverside
- 2. At each sampling location there are two hi-vol samplers to be used for sampling on each of eight sampling days. Each sampler is identified by a number from 1-6. One of them will sample continuously from 0700 hours PDT (7:00 a.m.) to 2100 hours (9:00 p.m.) and the second, with two hour filter changes as follows:

0700-0900 Pacific Daylight Time

0900-1100

1100-1300

1300-1500

1500-1700

1700-1900

1900-2100

If one of the two units is equipped with a recorder, this instrument will be used for the 14-hour sample.

3. Sampling will be conducted on July 8, 9, 10 and 11th. Four more sampling days will be selected during the following two weeks based upon the previous days smog forecast.

Jerry Sprung, Statewide Air Pollution Research Laboratory, (714) 787-3549, will obtain air pollution forecasts and will contact Jim Dudziak in Pasadena, (213) 796-9543, and Steve Heisler, (213) 795-6841, Ext. 1383 or 1389, who is in charge of Cal Tech's own sampling program the preceding evening if the following day is to be a sampling day.

4. Filters are packaged in aluminum foil lined folders. Each is pre-numbered on the filter edge and on the envelope. The envelope also includes a station, episode and filter type designation:

W X YYYY HR

W = C (Pasadena)

P (Pomona)

R (Riverside)

X = A, B, C...indicating successive l4-hour episodes YYYY = a four digit filter number

HR = an 8 \times 10 glass fiber (Gelman type A/E) filter As received in the field the episode designation is blank and must be filled in by the person changing filters.

Sample: R A 0128 HR

In this case the episode designation "A" is added to this and all other filters used on that day.

5. Filters should be handled lightly with clean hands (with gloves where hands will be dirty from climbing ladders) by the edges and installed with care, checking each filter for tears, holes etc. Any filter found to be damaged (except at the outer edge where it obviously will

not influence sampling or sealing of the filter) or which is dropped or otherwise contaminated should not be used. Defective filters should be so labelled on the outside of the envelope.

6. 14-hour sample

Record episode designation on filter envelope, the complete filter designation in log book, load filter, place clean recorder sheet in position, refill ink, verify that pen writes, record data and episode designation on chart, with coin or screwdriver set chart for 0700. Have these steps complete at least several minutes before 0700. Switch on at 0700 recording actual time to the nearest minute in log book (see sample log sheet). Shut off at 2100 hours recording time off in log book. Read and record initial and final flow reading from chart and staple chart to back of that day's log sheet. Operator initials log sheet as shown.

7. Two-hour sample (initial sample)

Record episode designation on filter envelope and load filter. At 0700 hours, switch on. After five minutes (needed for warm-up) record visifloat value at center of ball and enter this, with starting time in log book. At end of sampling period note and record visifloat value, shut off time and replace filter with fresh one. (For subsequent samples warm-up period unnecessary).

8. Removal and storage of loaded filters

Filters with atmospheric particulate matter are to be kept in storage

over dry ice or in a cold room at all times. After removing filter from hi-vol, replace in aluminum lined folder which, in turn, is inserted in an envelope and then into a large plastic bag kept sealed with a rubber band and then into cold storage. All filters from one day of sampling, including two-hour and l4-hour filters, go into the same plastic bag.

WARNING TO POMONA CREW: TRANSPORT DRY ICE CHEST IN TRUNK OF CAR AND HAVE WINDOWS OPEN AT ALL TIMES.

9. Return of filters and equipment to AIHL

After completion of sampling program, Art Alcocer will pick up (with assistance of field personnel) samplers and filters. The latter will be maintained at -80° C for transport back to the lab.

10. Supplementary data

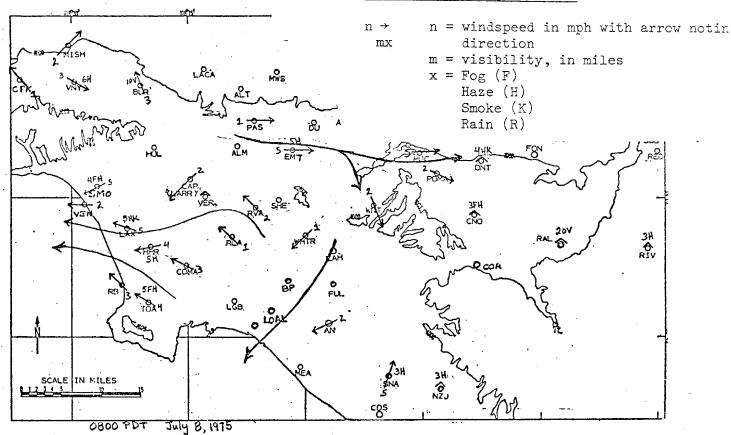
Pasadena

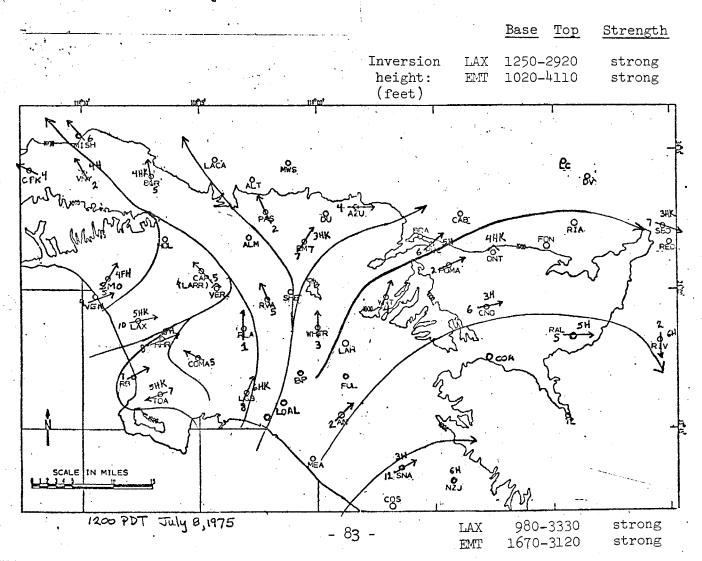
Jim Dudziak will calculate two-hour average ozone values from 60 instantaneous values printed out each two minutes. The two-hour periods will be the same as used for filter sampling. Steve Heisler will provide detailed instructions on reading these data from the ozone instrument. The O_3 data is recorded on the log sheet. Similarly Jim will calculate two-hour average $b_{\rm scat}$ values and record these in the log book. See sample log sheet.

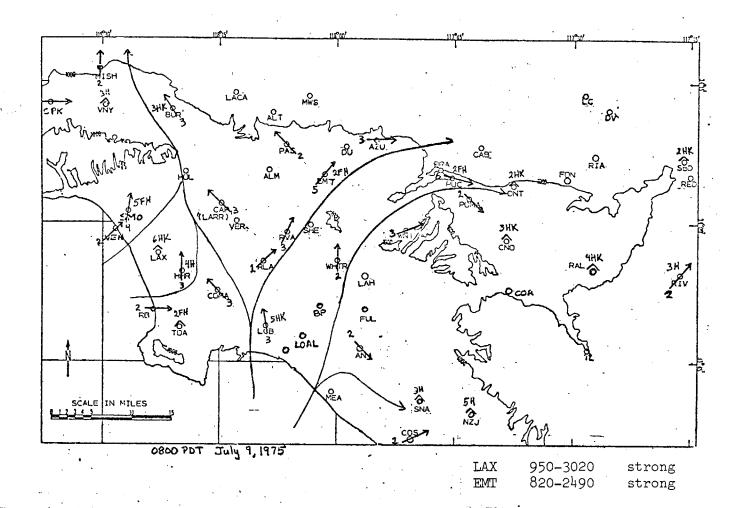
11. Contacts for questions

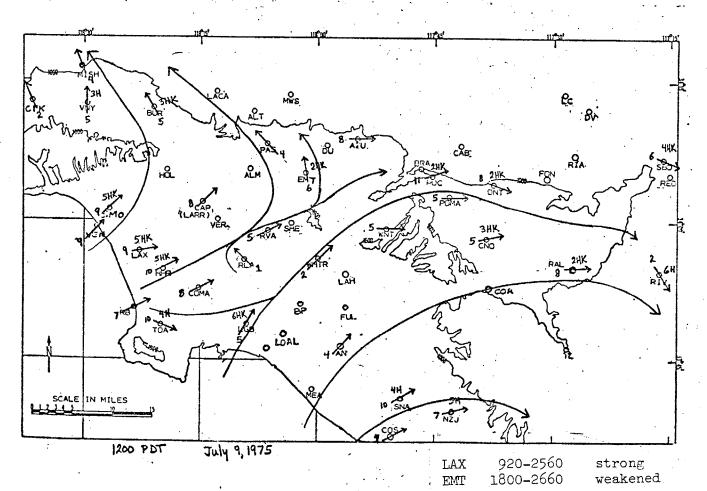
Call collect either Bruce Appel or Art Alcocer at (415) 843-7900.

Key to Meteorological Data

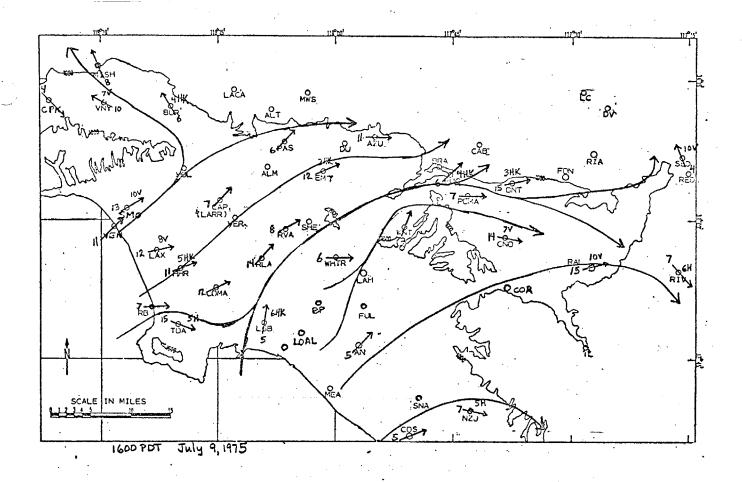


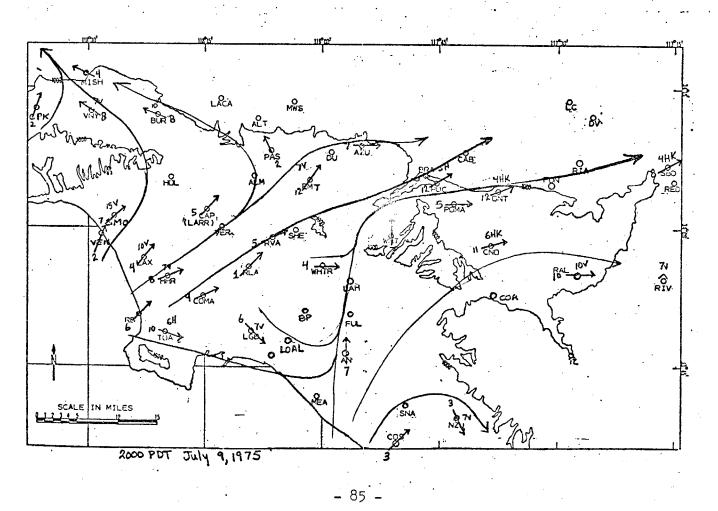


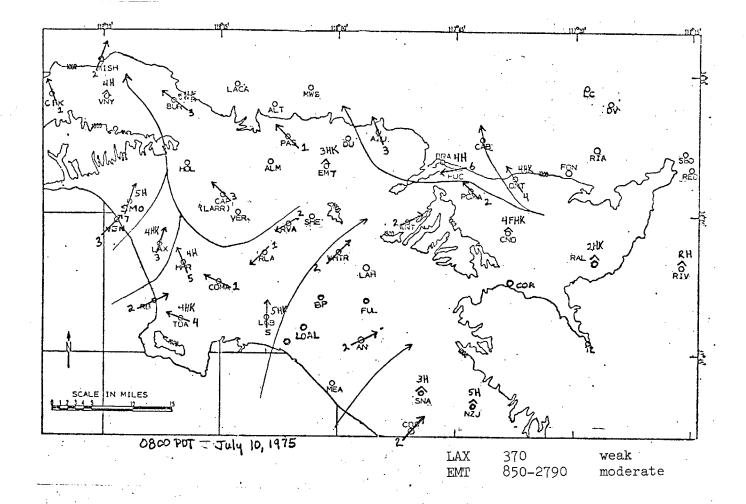


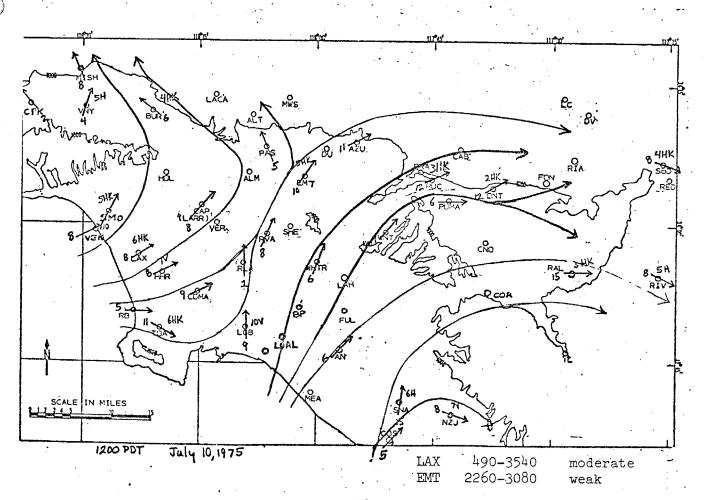


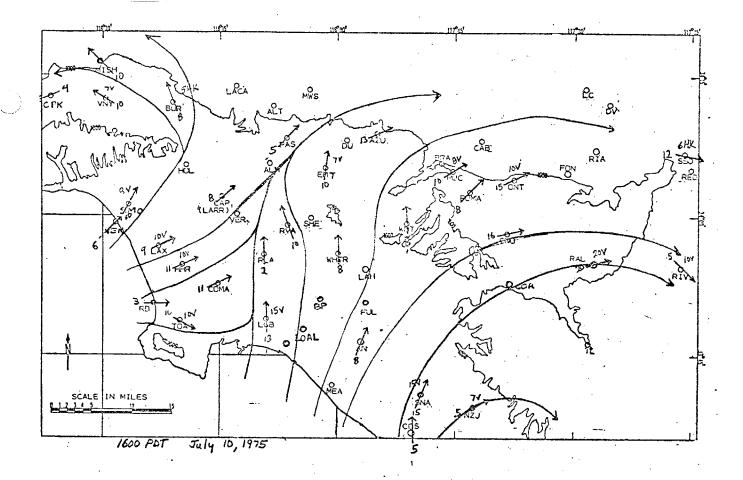
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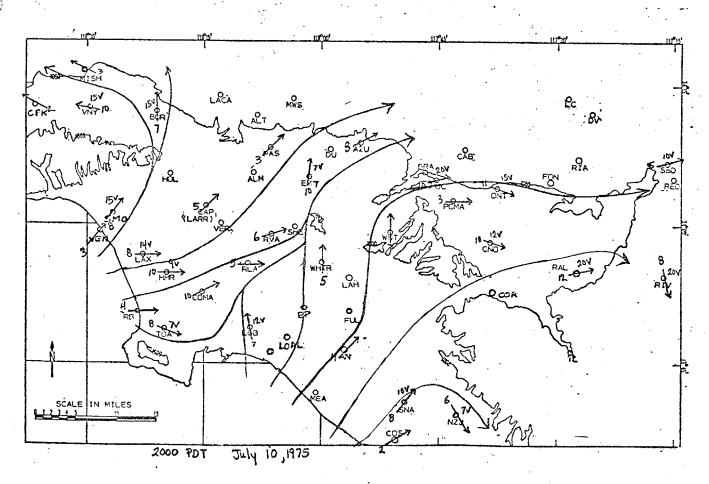


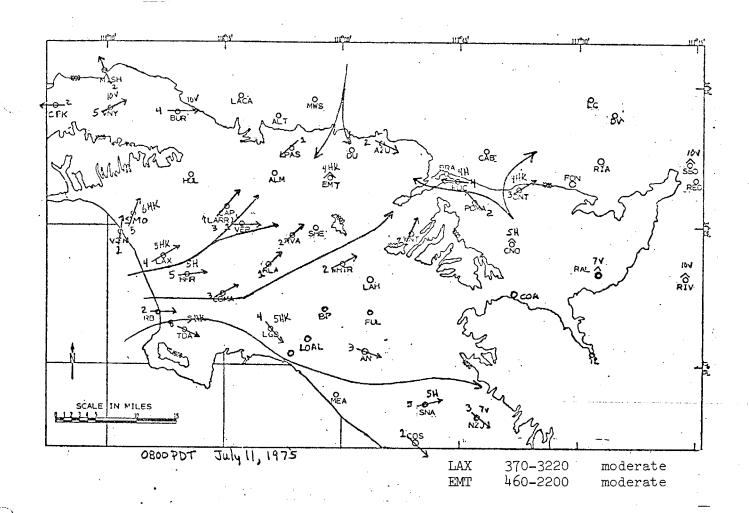


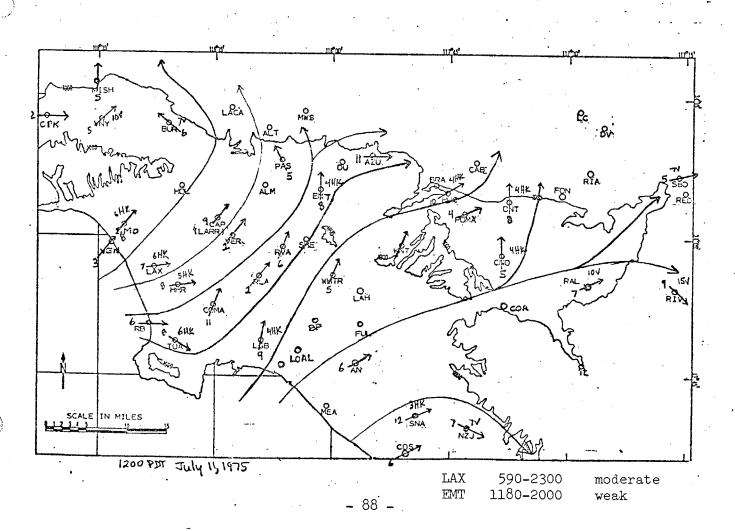


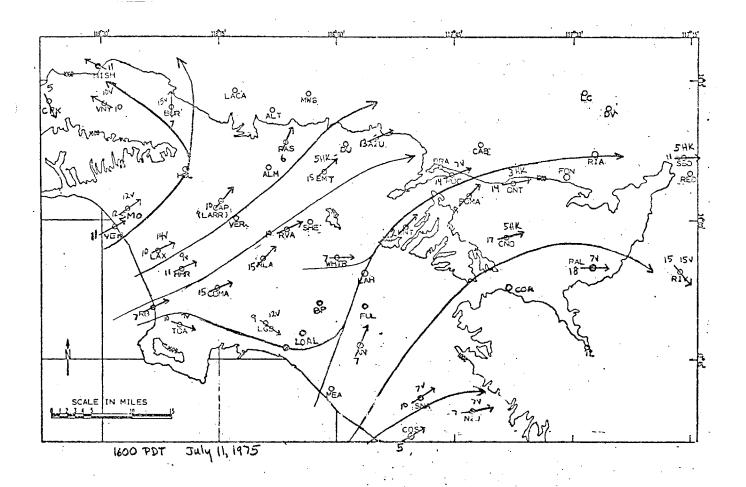


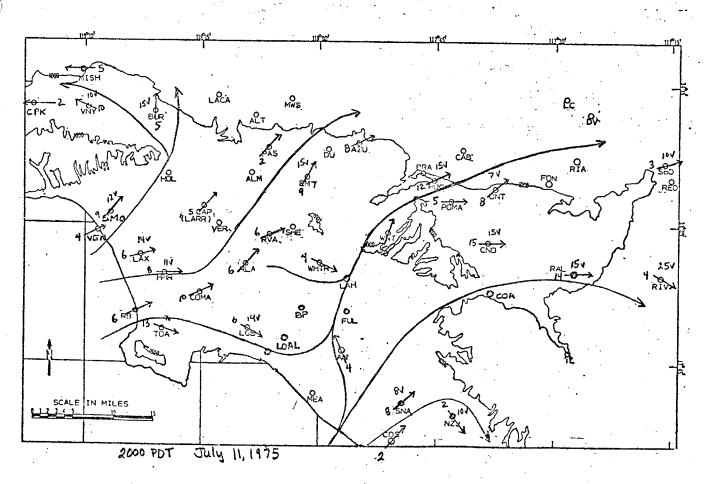


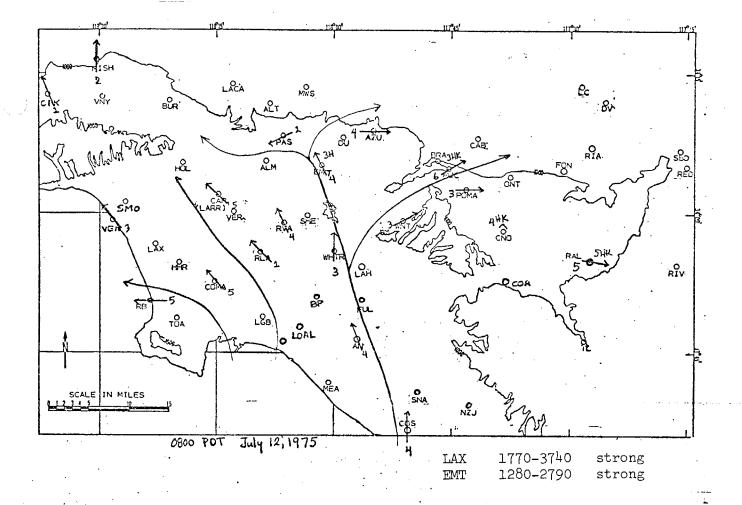


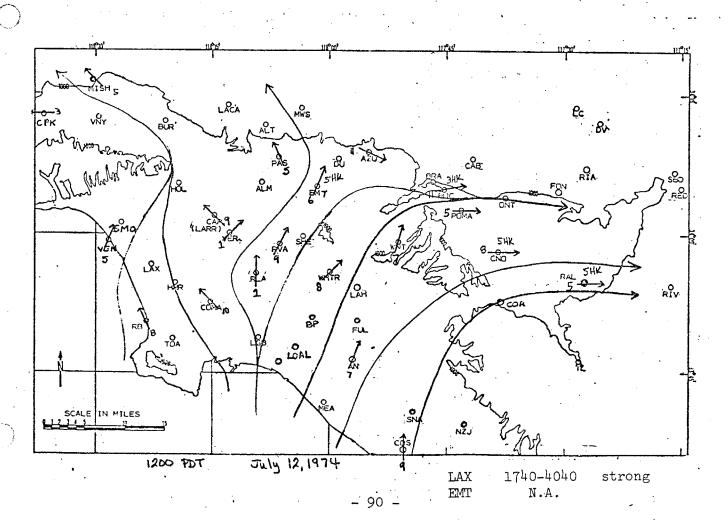




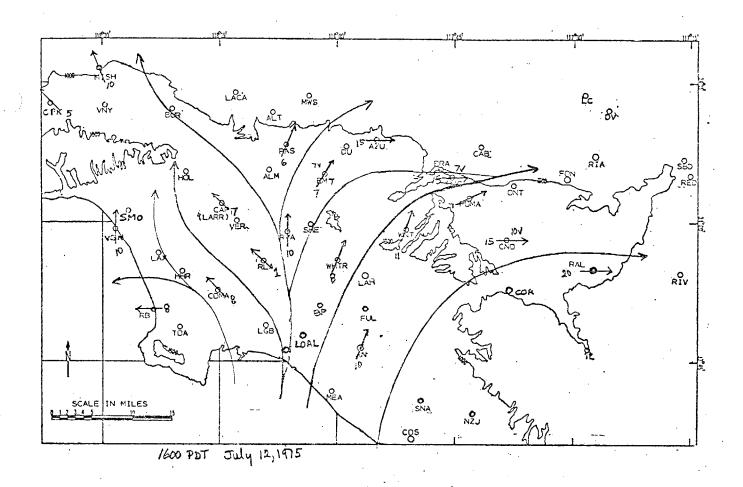


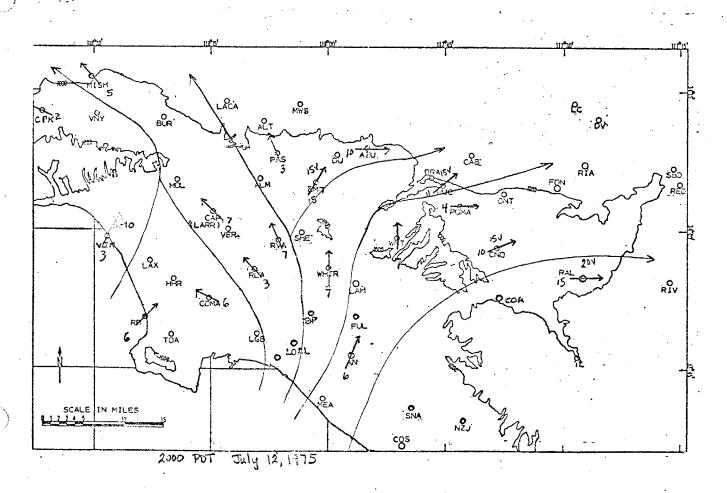


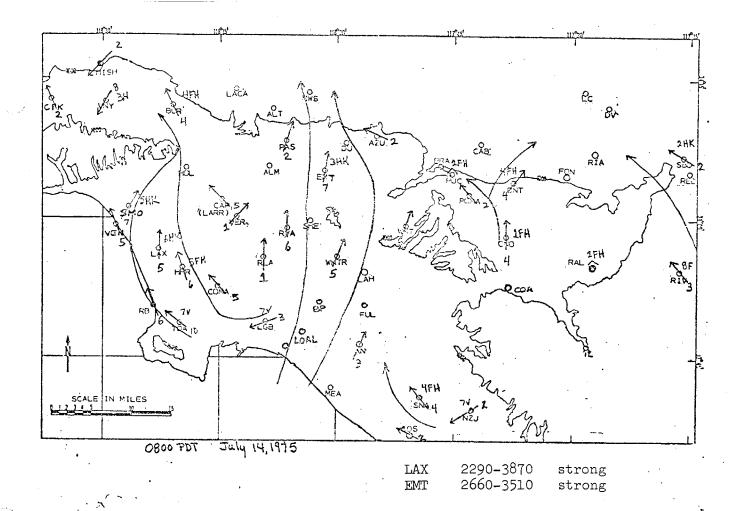


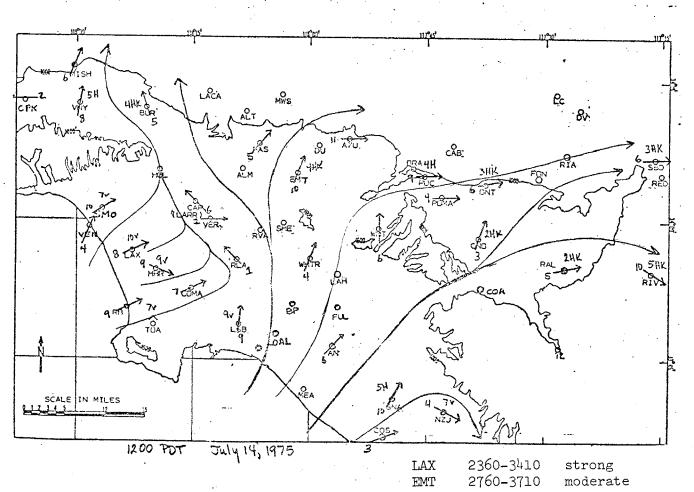


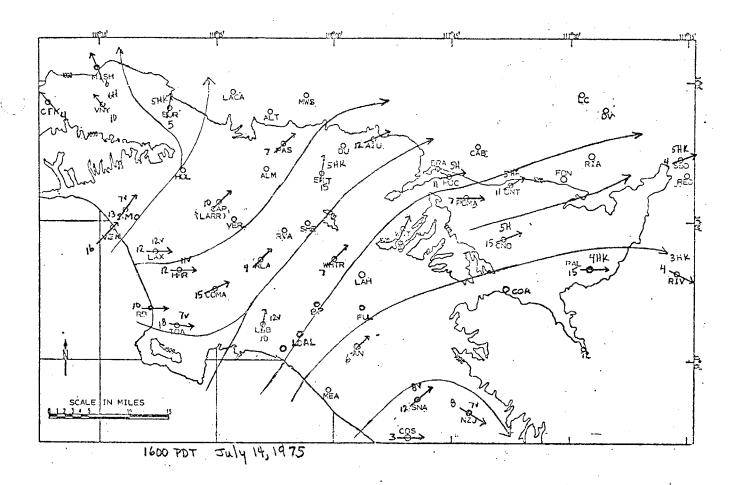
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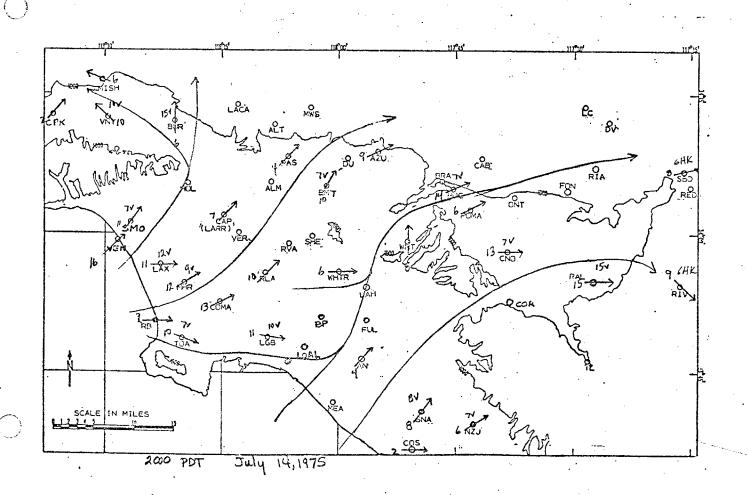


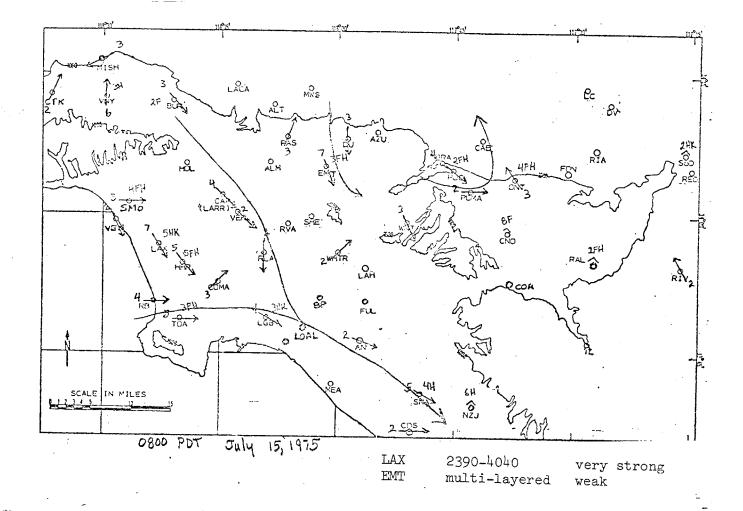


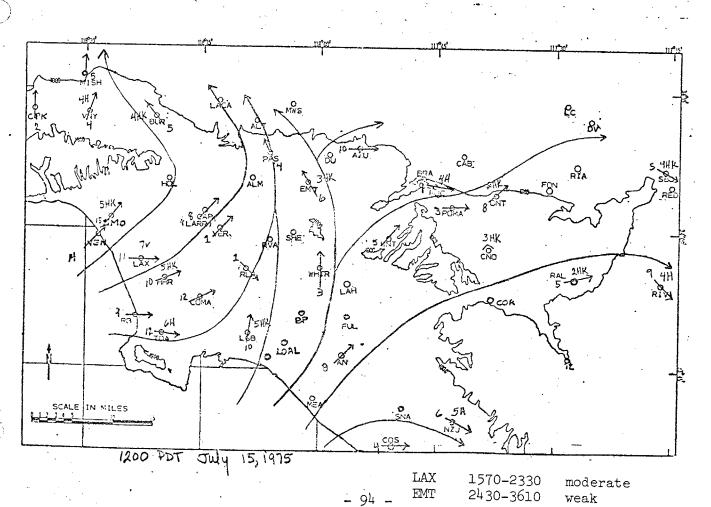


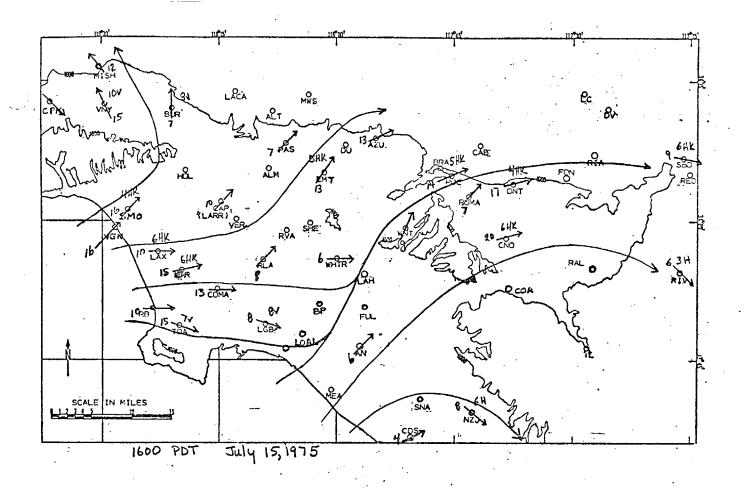


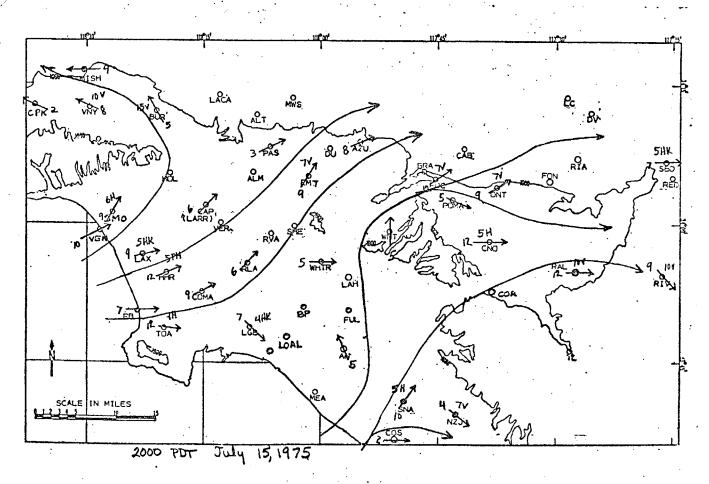


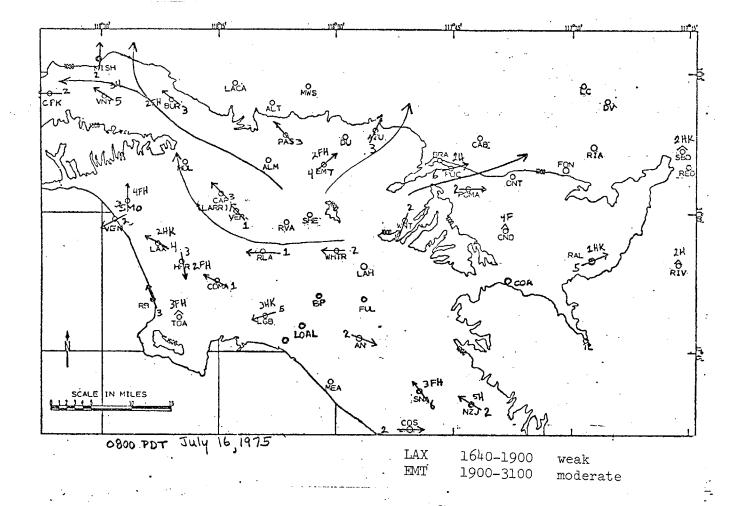


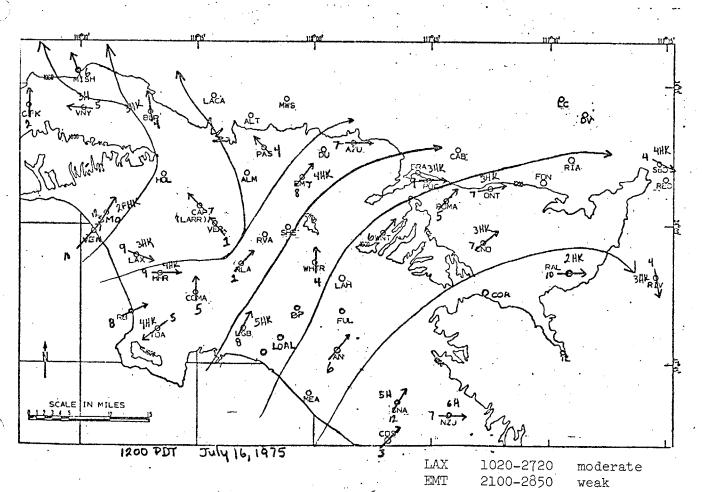


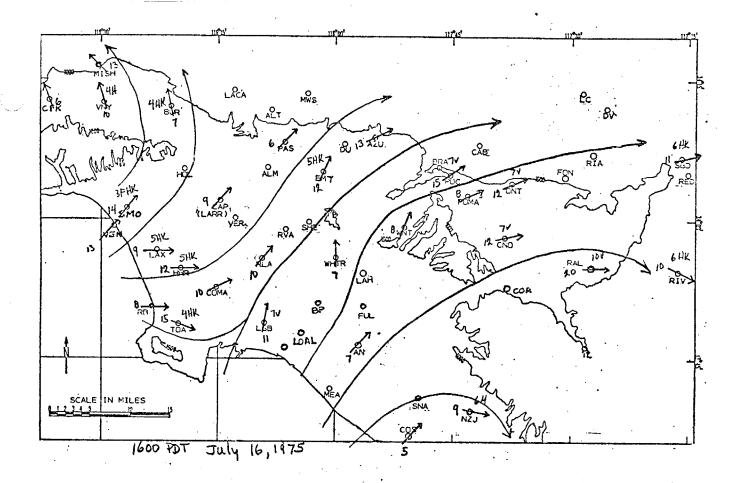


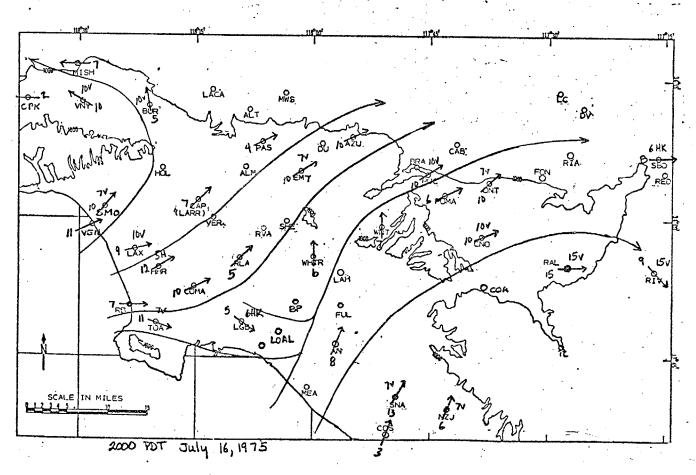












Appendix C

Description and Protocol of Procedure for Solvent Extraction, Evaporation and Carbon Analysis

Extractions were done for six hours in carefully precleaned Soxhlet extractors. Cycle time for all Soxhlets units was adjusted to be approximately 15 minutes. With the Soxhlets used for benzene followed by chloroform-methanol extractions, the filters were contained in prefired porous ceramic thimbles. Without the filtration provided by such thimbles, glass fibers from the filters plugged the pipets used for transferring the extract. No such thimbles were needed or used with the cyclohexane extractions.

The Soxhlet extraction was interrupted at a point in the cycle when ca. 5 ml of solvent remained in the extraction flask. This was transferred with washings to a 10 ml volumetric flask. After adjusting the volume to the mark, the contents were permitted to set undisturbed overnight to allow suspended material to settle. One ml aliquots were then removed from the clear solution and transferred, within a laminar flow clean bench, to combustion boats. The ceramic combustion boats were, themselves, resting in prefired nickel crucibles to minimize carbon contamination. Solvent was evaporated by drawing the air of the clean bench slowly over a set of four combustion boats in turn contained in specially-designed containers (Appendix C, Figure C-1). After two hours, the boats, in their nickel crucibles, were transferred to an empty vacuum dessicator and evacuated to ca. 1 mm Hg at room temperature for 30 minutes to remove final traces of solvent (Appendix D discusses the influence of evaporation and pumping time). The boats, in their crucibles, were then transferred to grease-free dessicators containing soda-lime and stored until analysis. Finally, the boats were transferred to the combustion tube of a carbon analyzer*, the carbon combusted to CO2, trapped and analyzed by gas chromatography with a thermal conductivity detector. A digital integrator was used for peak area determinations.

Each step in the handling and analysis of the samples was scrutinized and subjected to control experiments as part of the evolution of these procedures. These control experiments will be discussed in the quality assurance section.

The following includes protocols for the operations described above.

^{*}P. K. Mueller, R. W. Mosley and L. B. Pierce, J. Colloid Interface Sci. 39 235 (1972) and AIHL Method Number 30.

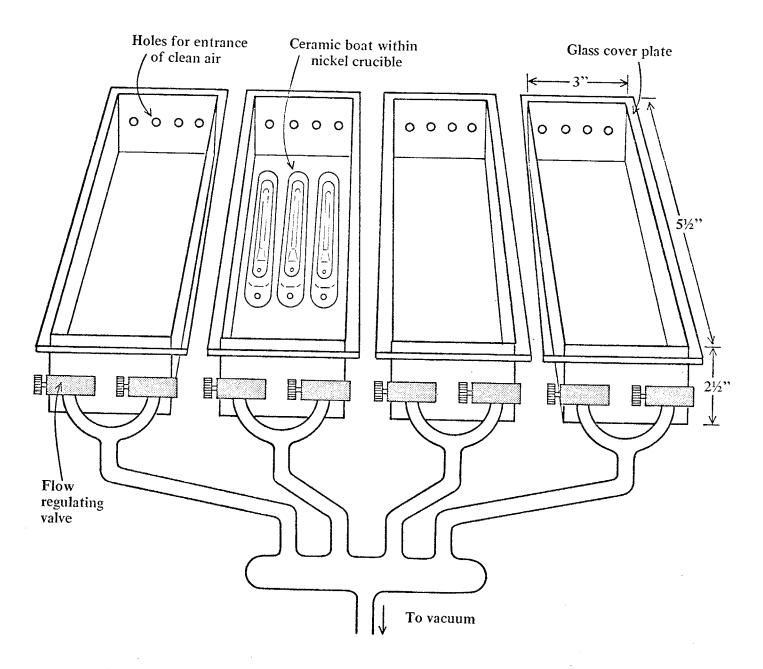


Figure C-1 Apparatus for solvent evaporation in clean air at room temperature (shown with boats in one unit).

PROTOCOL FOR DETERMINING CYCLOHEXANE, BENZENE AND METHANOL - CHLOROFORM SOLUBLE CARBON WITH GELMAN AE 8" \times 10" FILTERS

1. Cut filter diagonally in two parts (see Figure 10). Each half has three discs (1" diam) removed for Total Carbon, X-ray and Carbonate Carbon and four discs (1/4" diam) cut for M.S.T.A. determinations. Accordingly, 92% of each filter half remains for extractions.

2. Cyclohexane Extraction

- 2.1 Carefully wrap filter sample with solvent-washed copper wire before extraction. Pipet 5 ml of solvent into 125 ml flask. Connect flask to Soxhlet. Place sample in overflow unit and then carefully add solvent until it just overflows (ca. 55 ml). Wrap all joints tightly and cap unit with aluminum foil.
- 2.2 Extract for six hours in a hood. Control temperature with Variac. Adjust cycle time to 15 minutes with each unit.
- 2.3 After extraction, disconnect just before solvent is to siphon back. This will leave ≈ 5 ml of organic extract in the bottom of the flask.
- 2.4 Carefully transfer the ≈ 5 ml of organic extract to a clean 10 ml volumetric flask. Then rinse flask with a 1-2 ml portion of solvent and transfer to 10 ml volumetric flask. Repeat washings and transfer. When cool, bring to 10 ml mark with the solvent.
- 2.5 Transfer a one ml aliquot with MISCO pipet to the ceramic combustion boat (numbered and recorded).
- 2.6 Evaporate aliquots in boats to dryness by drawing air over samples for two hours in the evaporation set-up on clean bench (Figure B-1). Observe safety precautions particularly with benzene.
- 2.7 Take dried extracts and put in an empty vacuum desiccator (at room temperature) for 30 min. (l mm mercury) to remove residual solvent.
- 2.8 Following vacuum treatment, transfer samples to 0-ring sealed (grease-free) desiccators (< 4 samples per desiccator) over sodalime to minimize absorption of CO₂.
- 2.9 Analyze for carbon in the residue.
- 2.10 For 10% of all samples, repeat Steps 2.5 2.9 with a second aliquot of the same extract in a second boat for a duplicate determination.
- 2.11 Transfer the remainder of the 10 ml solution to a 20 ml bottle with aluminum foil lining in cap. Label and store.

3. Benzene Extraction

- 3.1 As in 2.1 but the filter is inserted into a porous ceramic thimble previously fired at 700°C to remove carbon. Then proceed as in 2.2 2.3.
- 3.2 Following benzene extraction, transfer extract to 10 ml vol. flask and save the pot flask (without further washing) for use in the MeOH-CHCl₃ extraction on the same filter.
- 3.3 Following benzene extraction, drain all possible benzene from Soxhlet, loosely cap bottom and top of Soxhlet, lay unit, still containing the solvent saturated filter, on an aluminum foil surface within the hood. Allow residual benzene to evaporate overnight.
- 3.4 Reassemble Soxhlet. For 14-hour filter samples, add 20 ml MeOH-CHCl3 to still-dirty pot flask and MeOH-CHCl3 in usual amount to Soxhlet and extract for six hours. Transfer to 25 ml flask. Evaporate 1 ml aliquots into boats.
 - For 2-hour filter samples add 8 ml MeOH-CHCl $_3$ to still-dirty pot flask, and MeOH-CHCl $_3$ in usual amount to Soxhlet and extract for six hours. Transfer to 10 ml flask. Proceed as in 2.5 2.11.
- 3.5 For 10% of all samples repeat steps 2.5 2.9 with a second aliquot of the same benzene extract.

4. Methanol-Chloroform Extraction

On the dried sample just extracted in (3), perform 2.1 thru 2.11 using 1:2 $\ensuremath{v/v}$ methanol-chloroform.

Appendix D

Calibration and Quality Assurance Studies

A. Carbon Determination

For analysis of carbon by combustion, the primary standard for instrument calibration was graphite. Graphite samples in the range 10-350 μg were weighed with a precision of \pm 1 μg using a Cahn electrobalance and combusted for this calibration. For daily calibration checks, a standard volume of $\rm CO_2$ was injected.

In the range 0-350 $\mu \rm g$, the least squares line relating graphite and CO₂ calibrations was:

Carbon (from graphite) = carbon (from CO_2) x 0.971 - 7.26

Validation of the calibration was further evidenced by the analysis of known amounts of potassium acid phthalate in aqueous solutions.

A particulate sample supplied by Euratom, Ispra, Italy, was distributed to numerous laboratories for analysis of species including carbon. The non-carbonate carbon value obtained by AIHL was 100% of the interlab mean for this sample.

For the routine carbon determination, a systematic check for instrument performance was built into the analytical protocol (Table D-1). At the beginning of each day, a check for leaks was done. Following this, a check for instrument stability was performed by analyzing 1 ml of CO₂ two consecutive times; the two readings had to agree within approximately 2%. Every five samples, or every two hours, a CO₂ standard was run to monitor the drift of the analyzer (ca. 2% per day). The data reduction technique included calculations to allow for this drift.

B. Study of Blanks

The observed values for each sample determination were corrected for blank values obtained with at least six pre-extracted filters. These filter blanks, however, incorporate numerous factors. For example, the solvent blank and blanks due to contamination of a combustion boat in handling. In the evolution of the analytical methodology, blank values were measured for such components which would later contribute to the observed filter blank values. Each solvent used was tested for non-volatile carbon residue by concentrating 200 ml aliquots to 10 ml in a Kuderna-Danish evaporator (Kontes K547300) followed by evaporation and analysis of 2 ml aliquots by the procedure given in Appendix C. This was essential to determine if further purification of the solvents was required. In the case of chloroform, redistillation proved necessary and did greatly decrease the solvent blank. Table D-2 summarizes results for solvent and combustion boat blanks with various treatments.

Table D-1

DAILY CALIBRATION AND QUALITY ASSURANCE PROTOCOL FOR CARBON ANALYZER OPERATION

Step 1 - Inject 1.00 ml CO2 at the loop (freeze trap). Proceed as follows:

Collection: 1 minute
Helium flush: 3 minutes
Warm-up: 2 minutes

Press injector valve and activate recorder and integrator. Record time (in 10-minute increments) and peak area.

Step 2 - Repeat Step 1.

- a. If Steps 1 and 2 agree within 6000 counts (or 1% of average peak area), proceed with Step 3.
- b. If Steps 1 and 2 differ by more than 6000 counts, check and clean the loop, check the valves, verify the GC performance.

Step 3 - Inject 1.00 ml CO2 at the combustion furnace. Proceed as follows:

Purge: 5 minutes
Combust: 10 minutes
Helium flush: 3 minutes
Warm-up: 2 minutes

Press injector valve and activate recorder and integrator. Record time and peak area.

- a. If result is $97 \pm 2\%$ of average peak area obtained in Steps 1 and 2, proceed with Step 4.
- b. If result is less than 95% of average Steps 1 and 2, check for leaks (glass connections, combustion tubes).
- Step 4 Analyze four samples using the same operating schedule as in Step 3. Record time and peak area.
- Step 5 Inject CO₂ at the loop as in Step 1. Proceed by alternating Steps 4 and 5. CO₂ at the loop should be checked at least every 2 hours.

Refer to AIHL Method 30 "Carbonate and Non-Carbonate Carbon in Atmospheric Particulate Matter", for operational details.

SOLVENT (NON-VOLATILE C) AND COMBUSTION BOAT CARBON BLANKS

Table D-2

Description	Number of Determinations	Mean $\frac{+}{2}$ 1 σ (μ g C)
Prefired boat (700°C)	8	1.30 + 0.4
Prefired boat, clean air flow for 2 hours, after 6 hours at < 1 mm Hg	8	1.89 <u>+</u> 0.3
Prefired boat, clean air flow for 4 hours, a 6 hours at < 1 mm Hg	4	2.40 <u>+</u> 0.5
Aluminum foil, ca. l in ²		3.83 <u>+</u> 1.1
Benzene ^c	14	3.09 <u>+</u> 0.4 per 40 ml ^d
Cyclohexane ^C	2	3.46 <u>+</u> 0.2 per 40 ml ^d
Methanol ^c	1,	16.3 <u>+</u> 2.4 per 40 ml ^d
Chloroform ^c	14	61.9 <u>+</u> 4.7 per 40 ml ^d
Chloroform, as above after redistillation	14	7.50 <u>+</u> 1.3 per 40 ml ^d

a. 700-800 ml/min.

b. Used for weighing and containing graphite in calibration

c. Matheson, Coleman and Bell "Spectroquality" solvent

d. 200 ml of solvent was condensed to 10 ml and from this 2 ml were evaporated to dryness and analyzed for carbon following the protocol given in Section IIIC. This is equivalent to the evaporation to dryness of 40 ml solvent.

Filter blanks were determined at three points in the study:

- 1. Immediately following the filter pretreatment by solvent extraction and high temperature drying, blank filters were checked for total carbon. This insured that further treatment was unnecessary before field use.
- 2. At the beginning of the development of extraction methodology to provide estimates of the limits of detections of the various solvent extracts based upon the variance of the blanks.
- 3. About halfway through the extractions of atmospheric samples. This was done using the exact protocols evolved for use with samples. These values were used to correct the atmospheric sample results and are summarized in Table D-3.

C. Loss of Organics by Evaporation

As described in Appendix C, following room temperature evaporation of solvents, the boats were placed in an empty dessicator and subjected to high vacuum (ca. 1 mm Hg) at room temperature to remove the residual solvent from the sample. In this process, there is a risk of losing the more volatile fraction of the residue. An experiment was conducted to establish the extent of such loss as a function of time in vacuum. The results are given in Table D-4. The maximum loss was about 10%. While the results suggest that room temperature evaporation of solvent was sufficient for its complete removal, a protocol involving 30 minutes under high vacuum was considered to provide an additional margin of safety without risk of significant loss of aerosol constituents.

D. Carbonate Carbon

Calcium carbonate was used to calibrate the analyzer against direct injections of $\rm CO_2$. The recovery of carbonate C average 88%. The validity of this calibration was demonstrated by analyzing 1" filter discs spiked with known quantities of $\rm Na_2CO_3$. Recovery of $\rm Na_2CO_3$ from filter discs was found to be 86 + 19%.

E. Precision Studies

The observed precision reflects a number of factors including the reproducibility of the extractions, evaporation, carbon determination and the homogeneity of deposition of carbon across the filter. In some cases, these parameters were evaluated independently, but in general, the resulting variance reflected their combined of ributions.

The experimental design and results are as follows:

1. Precision of the total carbon (CEL) determination

Two 1" discs were punched out of every filter in the four episodes to be studied and analyzed for CEL. The discs came from opposite halves

Table D-3

FILTER BLANKS FOR PRETREATED GELMAN AE GLASS FIBER FILTERS

Species	μ g C/cm ² a
Total carbon (CEL)	2.41 <u>+</u> 0.18 ^b
Cyclohexane extractable C (CEC)	0.24 <u>+</u> 0.081
Benzene extractable C (BEC)	0.094 + 0.012
Methanol-chloroform extractable C (MCC)	0.52 <u>+</u> 0.10

a. Mean of six samples \pm 1 σ

b. Compares to 3.3 \pm 0.2 for Gelman AE filters as purchased.

LOSS OF EXTRACTED ORGANIC AEROSOL CARBON AS A FUNCTION OF TIME IN VACUUM (ca. 1 mm Hg) AT ROOM TEMPERATURE

Table D-4

Sample ^{a,b}	Sampling Site	0	2	Fime (minute	,	260
		<u>-</u>		μg carbon	180	360
CEC	Pasadena	116.4	115.4	114.0	106.3	106.6
BEC	Riverside	102.4	104.0	105.7	101.8	97.6
MCC	Riverside	156.0	162.6	161.5	160.2	150.5

a. See Table 5 for explanation of terms

b. This experiment used 14-hour filter samples collected July 16, 1975 on a day of moderate smog (ozone 0.2 ppm).

of each filter (see Figure 9). The results of ten randomly selected sets of duplicates were statistically evaluated and used as a measure of precision for CEL (see Table D-5). The resulting coefficients of variation ranged from 2 to 3% with somewhat better results for 14-hour compared to 2-hour samples.

2. Precision of the solvent extractable carbon determinations

2-hour and 14-hour filter samples were cut into two or more equal area sections. Two equivalent sections from a number of filters were extracted in cyclohexane or benzene followed by methanol-chloroform. The results expressed as pooled coefficients of variation are also given in Table D-5. As expected, the 14-hour samples lead to generally better precision than the 2-hour samples. The poorest results were for cyclohexane extractable carbon on 2-hour samples which exhibited a C.V. of nearly 16%. This is consistent with the low level of cyclohexane extractable carbon observed which ran as low as about 10 $\mu\rm g$ per aliquot analyzed.

3. Precision of evaporation and carbon determination

Randomly selected extracts representing about 12% of all the extracts in each solvent system were reanalyzed by evaporating a second aliquot from the same extract. The second analysis was done on a separate day, included in a new batch of samples. This "blind" reanalysis minimized any bias associated with special handling. The precision results, expressed as pooled coefficients of variation, are given in Table D-6. The low level of CEC in a 1 ml aliquot (i.e., 10%) of the extract suggested that it might be better to evaporate two 1 ml aliquots into the same crucible. The additional possibility for contamination and longer (e.g., 4-hour vs. 2-hour) time need for evaporations suggested this be done only if essential.

To test this, a set of 14 samples containing from 12 to 32 μg CEC per 1 ml aliquot were reanalyzed using 2 ml (i.e., 20%) of the extract. The results, in μg CEC per 1 ml, agreed on average within 2% of the value obtained with 1 ml. Accordingly, no change in protocol was made.

4. Uniformity of carbon deposition

While an upper limit to non-uniformity is included in the value quoted for the precision of CEC in Table D-5, an independent and more detailed study of this was done. A single 8 x 10" 24-hour glass fiber sample collected in Berkeley was used to supply ten 1" discs chosen to represent the complete filter. Analysis of these discs for CEL exhibited a C.V. of 2.3%, suggesting good uniformity of deposition. Furthermore, this result is in good agreement with the C.V. value 1.9% found for CEL in 14-hour samples (2 discs per sample) as given in Table D-5.

Table D-5
PRECISION OF CARBON DETERMINATIONS

<u>Determination</u> ^a	Sampling Time Hours	Number of Duplicates b	Pooled Coefficient of Variation of Duplicates
CEL	2	10	2.6
CEL	14	10	1.9
CEC	2	3	15.5
CEC	14	3	4.7
BEC	2	7	11.8
BEC	14	5	4.2
MCC	2	5	3.3
MCC	14	6	10.3

a. See Table 5 for explanation of terms.

b. Refers to duplicate sections cut from the same filters.

Table D-6 Precision of Evaporation and Carbon Determination of Solvent Extracts

<u>Determination</u> ^a	Sampling Time, Hours	Number of <u>Duplicates</u> b	<u>C.V. (%)</u>
CEC	2	9	8.6
CEC	14	3	0.2
BEC	2	9	10.6
BEC	14	3	6.0
MCC	2	9	11.9
MCC	14	3	3.6

a See Table 5 for explanation of terms.

b Refers to duplicate evaporations of 1 ml aliquots from the same extracts.

F. Loss of Bromine During X-Ray Fluorescence Analysis

One-inch disc filter samples, stored in a freezer until ready for analysis, were analyzed for Pb and Br by a Philips Model PW1410 wavelength dispersive x-ray spectrometer at atmospheric pressure, 58 kv and 40 ma current. Since some bromine loss was expected, multiple analyses were done on a well-loaded sample.

Table D-7 details the results for both Pb and Br. Over a period of 1 hour, a bromine loss of 25% was observed while Pb remained constant. These results suggest a loss of, at most, several percent in bromine during the initial analysis (plotting Br vs. mid-point times and extrapolating to zero indicates about a 3% loss).

G. The Precision of the MSTA Technique

Precision for MSTA analyses was established by replicate determinations (on separate days) of three of the 2-hour samples collected in Riverside during the July 9 episode. The results are shown for each identifying fragment (Table 6 lists identifying fragments and probable structures, where known, for constituents discussed in this report) separately for compounds present above and below 0.1 $\mu\text{g/m}^3$. (Table D-8 and D-9) The combined coefficient of variation for all materials is close to 50% in both cases with precision for higher concentration somewhat better.

H. Comparison of Organics Recovered by Solvent Extraction-Carbon Analysis and MSTA

In an effort to compare the total organics observed by MSTA with those obtained by the solvent extraction-carbon determination, the total $\mu g/m^3$ for all compounds and/or fragments measured by MSTA was calculated for the 14-hour samples. Since this total includes the elements H, O, N, S and possibly others, in addition to carbon, these totals are only proportional to the carbon present. For the 13 most abundant compounds determined by MSTA (see Table E-2) the average carbon content was 60%. Using this value as approximately applicable to the total organics by MSTA permits an approximate comparison with solvent extraction-carbon analysis.

Table D-10 compares the total extractable carbon, as measured by the sum of benzene and methanol-chloroform extractable carbon, with the total organics by MSTA. The ratio of MSTA total organics to total extractable carbon is relatively constant at about 0.5. Assuming the organics observed by MSTA to be 60% carbon, MSTA is seen to account for about 30% of the soluble carbon.

The comparison given in Table D-10 is limited because of the possibility of thermal decomposition of the polar organics (leading to non-volatile carbonaceous material) present in the samples during the MSTA. In an effort to minimize this factor, Table D-11 compares the organics observed by MSTA and solvent extraction carbon analysis employing analyses done on cyclohexane extracts. Since in this solvent the abundance of polar organics is reduced, we presume that effects of thermal decomposition would be minimized. This solvent may also minimize the extraction of high molecular weight organics which would not volatize at $\leq 380\,^{\circ}\text{C}$ in vacuum. As shown in the table, MSTA

Table D-7

LOSS OF BROMINE WITH TIME UNDER X-RAY ANALYSIS
CONDITIONS FROM PARTICULATE SAMPLE ON GLASS FIBER FILTER DISC

Time Minutes	Br <u>(µg/cm²)</u>	Pb <u>(ug/cm²)</u>
0- 9	0.72	5.6
9-18	0.68	5.9
18-27	0.65	5.9
27-36	o . 63	5 . 9
36-45	0.63	5.9
45-54	0.60	5.6
54-63	0.54	6.0
	Me	an 5.8 ± .2

Filter No.: ^a Trial:	RB4741	<u>1R</u> 2	<u>RB+75</u> 1	<u>HR</u> 2	<u>RB478.</u>	HR 2_	C.V.(%)
C_5H_{11} C_5H_9							
$ C_{\gamma} H_{\gamma} C_{B} H_{10} C_{9} H_{12} C_{9} H_{10} $.03 .028	.02	.06 .054 .032	.06 .030 .020	.031	.057	28.3 23.6 58.0 32.6
$C_{10} H_{8}$ $C_{8} H_{8}$ $C_{11} H_{10}$ $C_{11} H_{13}$ $C_{6} H_{5} O$.042 .042	.021 .0096	.0081	.0018	.032 .053	.015 .096 .003	51.2 53.3 88.8 94.3
Congress of the congress of th	.09 .074 .038 .053	.063 .066 .030	.006 .043 .022 .041	.026 .031 .005 .026	.11 .081	.026 .063 .042	69.0 16.7 89.0 36.9 49.5
$C_{2}H_{4}O_{2}$ $C_{4}H_{5}O_{2}$ $C_{5}H_{8}O_{2}$ $C_{6}H_{10}O_{2}$ $C_{6}H_{10}O_{4}$ $C_{9}H_{10}O_{2}$.022	.01	53.0
C ₂ H ₂ N CHNO C ₄ H ₉ N ₂ C ₅ H ₈ O ₃ C ₆ H ₈ O ₂ C ₇ H ₁₀ O ₂ C ₃ H ₅ O ₃ C ₅ H ₁₀ O ₃ C ₅ H ₉ NO ₄ C ₅ H ₉ NO ₅	.104	.068			.12	.059	29.6 - 48.2
Sulfates NH ₄ Cl NH ₄ NO ₃					.06	.021	68.1

Combined: 51.3^b
a. Samples used were collected in Riverside, Episode B (July 9, 1975).

b. Excludes inorganic compounds. - 113 -

Filter No.: a Trial:	<u>RB4</u> 1_	7 ¹ +HR 2_	<u>RB4</u> _1_	75HR 2	<u>RB4</u> 1	78HR 2	C.V.(%)
C_5H_{11} C_5H_9	.25 .69	•25 •53			•32 •90	.15 .51	35.1 32.1
$C_{\gamma}H_{\gamma}$ $C_{8}H_{10}$	·31	.20	.43	.21	.28	.09	50.1
C _g H ₁₁ C _g H ₁₂ C _g H ₁₀	.18 	.093 	 				45.1
$C_{10}H_{g}$ $C_{g}H_{g}$ $C_{11}H_{10}$.25 	.11					55.0
$C_{11}H_{13}$ $C_{6}H_{5}O$ $C_{5}H_{6}O$ $C_{6}H_{6}O_{2}$ $C_{7}H_{6}O$	-35 	.2 ¹ 4 	•56 	.19 	•37 	.021 	73.6
CyH ₃ O CyH ₁₂ O					~ ··		
$C_2H_4O_2$ $C_4H_5O_2$ $C_5H_8O_2$ $C_8H_{10}O_2$ $C_6H_{10}O_4$ $C_9H_{10}O_2$.63 2.1 1.8 .37	.68 1.9 1.9 .89	.83 1.8	.56 3.8	.72 2.6 3.1 1.3 4.1	.83 1.7 1.4 .99 1.4	17.1 22.2 46.6 34.1 69.4
C ₂ H ₂ N CHNO C ₄ H ₃ N ₂ C ₅ H ₃ O ₃	•5 3•5	.19 2.5	3.9 4.6 0.70	3.9 3.8 .056	.38 4.8	.29 3.5	8.6 19.7 120
C ₆ H ₃ O ₂ C ₇ H ₁₀ O ₂ C ₈ H ₅ O ₃ C ₅ H ₁₀ O ₃ -C ₅ H ₉ NO ₄ -C ₅ H ₉ NO ₅	.74 .29 1.0	1.0 .30 2.9	.77 2.5 .26	.94 1.3 .077	.67 .55 1.4	.76 .29 1.6	16.2 36.4 38.2 76.8
Sulfates NH ₄ Cl NH ₄ NO ₃	5.9 3.6	4.2 3.2	5.1 2.1	4.7 3.2	4.2 .54 2.1	2.8 .26 1.5	20.4 22.9 23.6
						Combined:	45.6 ^b

a. Samples used were collected in Riverside, Episode B (July 9, 1975).

b. Ex ${f c}$ ludes inorganic compounds.

Table D-10

COMPARISON OF ORGANICS RECOVERED BY SOLVENT EXTRACTIONCARBON ANALYSIS WITH TOTAL ORGANICS BY MSTA

Episode	Station	Total Extractable Carbon $(\mu g/m^3)^a$	Total Organics by MSTA $(\mu g/m^3)$		rganics by MSTA ctractable Carbon
7/9/75	Pasadena	20.9	11.6		0.56
7/9/75	Pomona	19.1	10.4		0.54
7/9/75	Riverside	16.8	6.7		0.40
7/10/75	Pasadena	17.5	10.6		0.60
7/10/75	Pomona	16.1	8.4		0.52
7/10/75	Riverside	11.0	6.2		0.56
				Mean:	0.53 + 0.07

 $\frac{\text{Total carbon by MSTA}^{b}}{\text{Total extractable carbon}} = 0.3$

a. The sum BEC + MCC

b. Assuming organics to be 60% carbon (see Table E-2)

Table D-11

COMPARISON OF TOTAL ORGANICS IN CYCLOHEXANE EXTRACTS
BY MSTA WITH CYCLOHEXANE EXTRACTABLE CARBON

Episode	<u>Station</u>	Cyclohexane Extractable Carbon (µg/m³)	Total Organics by MSTA $(\mu g/m^3)$	Total Organics by MSTA Cyclohexane Extractable C
7/9/75	Pasadena	6.3	6.1	0.97
7/9/75	Pomona	6.5	7.5	1.15
7/9/75	Riverside	14.14	3.2	0.73
7/10/75	Pasadena	4.1	3.6	0.88
7/10/75	Pomona	5.6	2.8	0.50
7/10/75	Riverside	2.9	2.2	0.76
				0.83 <u>+</u> .22

$$\frac{\text{carbon by MSTA}^{a}}{\text{cyclohexane extractable C}} = 0.6$$

a. For the 6 most abundant compounds in the cyclohexane extracts the % carbon averaged 70%. This ratio assumes this value.

appears to recover about 60% of the cyclohexane extractable carbon. The 40% difference may be relatable to errors in MSTA response factors. Work is continuing to improve the accuracy of the MSTA technique.

Appendix E

MSTA Data for Filter Samples

The minimum response that can be measured by MSTA (Area = 1000), converted into minimum detectable concentration, is different for each compound, amount of sample analyzed, and instrument sensitivity on the day analyzed. Table E-l lists minimum detectable concentrations, in $\mu g/m^3$, for compounds with Response Factor (R.F.) values of 1.0. Minimum detectable concentrations for all the compounds discussed in this report may be obtained by dividing the values shown in Table E-l by the R.F. values listed in Table 6 (p 28). Minimum concentrations for reliable quantitation are approximately four times the minimum detectable values.

Table E-2 lists the 13 most abundant compounds and/or fragments observed in ambient samples in order of decreasing abundance. Table E-3 lists the fragments observed in blank Gelman AE filters and the ratio of peak areas in a typical 2-hour sample to the level on the blank. In general, the blank correction represents a small fraction of the observed peaks. The notable exceptions include $\rm C_7\,H_7\,NO_4$ (a possible toluene oxidation product) and $\rm C_5\,H_9\,NO_5$, identified as an acid nitrate.

Table E-4 compiles the diurnal changes in concentration for all compounds and fragments determined by MSTA. Data missing from the compilation are indicated by either a dash (-) to indicate no mass fragment detected, or a zero (0) to indicate nothing left after subtracting filter blank.

Table E-1 MINIMUM DETECTABLE CONCENTRATIONS BY MSTA FOR COMPOUNDS WITH RESPONSE FACTOR 1.0 $(\mu g/m^3)^a$

Time	Pasa	dena	Pom	ona	River	Riverside			
(PDT)	July 9	July 10	July 9	July 10	July 9	July 10			
7-21	.026	.025	.026	.026	.022	.022			
7- 9	.17	· 04	.076	.10	.040	.10			
9-11	.12	.04	.10	.10	.040	.083			
11-13	.043	. 04	.10	.10	.050	.10			
13-15	.18	.04	.10	.050	.10	.083			
15-17	.18	.04	.10	.10	.027	.077			
17-19	.18	.04	.10	.10	.083	.077			
19-21	.12	• 014	.10	.10	.083	.0110			

a. Divide the numbers given by the Response Factor (Table 6) to get minimum detectable concentrations for other compounds.

Table E-2

ORGANICS LISTED IN APPROXIMATE ORDER OF DECREASING

ABUNDANCE IN AMBIENT SAMPLES

Fragment	Rank	Probable Structure	% Carbon
$C_4H_8O_2$	1	pentanedioic acid	45
C5 Hg O2	2	hexanedioic acid	49
C ₈ H ₅ O ₃	3	phthalates	67
$C_6 H_{10} O_2$	14	methylhexanedioic acid	53
CHNO	5	?	ca. 70
C2H4O2	6	total acids	> 40
$C_5 H_9$	7	total alkanes	87
C_2H_2N	8	?	> 60,
C4H8 N2	9	?	57
$C_4H_9N_2$	10	?	56
C3H ₅ N2	11	?	> 57
$C_5 H_{10} O_3$	12	?	51
$C_5H_{\gamma}NO_4$	13	?	41
		Mea	n: 58 ^a

a. Excludes lower limit values.

	Gross Amount Detected a Blank Amount
C_8H_{13} Alkanes, high mw C_8H_{11} Alkenes, med mw C_8H_{11} Alkenes, high mw	4 14 4
C_7H_8 O Hydroxytoluene + Benzyl Alcohol CONH C_4H_8 N_2 C_7H_7 NO_4	5 5 5 1
$C_8 H_5 O_3$ Phthalates $C_5 H_9 NO_5$	12 2
C5H5Cl Heptachlor?	1

a. In a typical 2-hour sample.

Table E-4

MSTA DATA FOR FILTER SAMPLE

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Pasadena (Caltech)

		Z C	ALIPHATIC HYDROCARBONS								
TIME (PDT)	C ₅ H ₁₁ Total Alkanes	C ₆ H ₁₃ Alkanes, Low Molec	C ₆ H ₁₃ Alkanes, Med MW	C ₆ H ₁₃ Alkanes, High MW	C ₅ H ₉ Total Alkenes	C ₆ H ₁₁ Alkenes, Low MW	C ₆ H ₁₁ Alkenes, Med MW	C ₆ H ₁₁ Alkenes, High MW			
7-21	.19	.05	.074	.009	.49	.028	.16	.107			
7-9	.30	.03	.07	-	.51	0	.20	.033			
9-11	.36	.10	.10	-	.68	.07	.18	.07			
11-13	.28	0	.10	.11	.72	0	.15	. 34			
13-15	.20	0	.15	.037	.88	.05	.26	.15			
15-17	.20	0	.11	-	.81	0	.25	.14			
17-19	.01	-	0	-	.46	.009	.18	.06			
19-21	.10	0	.076	-	.42	.023	.19	.07			

	zenes	zenes	AROMAT I	C HYDROC	CARBONS
TIME (PDT)	C ₇ H ₇ Xylenes, Alkyl Ben;	C ₈ H ₁₀ Xylenes, Ethyl Ben	C ₉ H ₁₁ Alkyl Benzenes	C ₉ H ₁₂ A1kyl Benzenes	C ₁₀ H ₁₄ A1ky1 Benzenes
7-21	.19	.047	.096	.040	.0043
7-9	.06	-	-	_	-
9-11	.35	0	.175	-	- '
11-13	.19	.087	.102	.063	.058
13-15	.27	-	~	.025	_
15-17	.11	.091	.075	_	-
17-19	.07	-	0	_	_
19-21	.13	-	.002	-	_

	POLYCYCLIC HYDROCARBONS														
TIME (PDT)	C ₈ H ₈ Tetrahodro-	naphthalene	C ₉ H ₁₀ Indan	C ₁₀ H ₈	Naphthalene	C ₁₀ H ₁₈ Perhydro-	naphthalene	C ₁₁ H ₁₀ Methvl-	naphthalenes	C11H13 Dimethyltotra	hydronaphthal	C ₁₄ H ₁₀ Anthracene &	Phenanthrene	C ₁₆ H ₁₀ Pyrene & Isomows	
7-21	.06	51 .	.0049	.01	.6	.04	1	_		.008		.001		_	
7-9	-		~	~		_		_		_		.091	.0		
9-11	-		-	,00	24	_		_		.017	7	_		-	
11-13	.10		011	.00	8	.01	9	_		.007		_		_	
13-15	.02	6		.02	0			_		_		_		_	
15-17			-	.01	9	_		_		_		_		_	
17-19	7		7	~		_		_		_		_			
19-21	.03	9	-	.0058				.01	4	-		_		-	
	le?			IATED	ARO	MATIO		1		ene + nol	r	- Ou	ı		
TIME (PDT)	C ₆ H ₄ O ₂ Benzoquinone?	C ₆ H ₅ O Phenol +	NO ₂ ,CHO,COOH?	L ₆ H ₆ U Phenol	C ₆ H ₆ O ₂	benzenes	C ² H ⁶ O	benzaldenyde Interference	C ₇ H ₈ O	Hydroxytoluene Benzyl Alcohol	C9H ₁₂ 0	rimetnylpne + Isomers	C ₁₂ H ₁₀ O ₂ Biphenol	C ₁₄ H ₂₁ 0	Ulbutyl- methylphenol
7-21	-	.014	1.	021	.08	3		-	.04	19	.02		.015		088
7-9	-	.02		-	-			-	_		_		_		
9-11	~	-		07	. 16			-	.04	15	.03	34	_		_
11-13	-		. (004	.10		()	.03	36	.01	0	-	-	-
13-15	-	_	()	.05	3	•	-	.13	3	. 04	6	_	_	-
15-17	-	. 14	. (006	-		-	-	.00)8	.11		_	_	
17-19	-	.10	•	-	-		-	•	.01	.1	_			_	
19-21	-	-	()	.01	4	-	•	0		_		_	_	

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Pasadena (Caltech)

				ojc	(CARBOXYL	IC ACIDS		Ö
TIME (PDT)	C ₂ H ₄ O ₂ Total acids (as Acetic)	C ₄ H ₆ O ₂ Pentanedioic Acid	C ₅ H ₈ O ₂ Hexanedioic Acid	C ₆ H ₁₀ O ₂ Methylhexanedi Acid	C ₇ H₅O Benzoyl Ion	C ₇ H ₆ O ₂ Benzoic Acid	C ₈ H _{8O₂ Methylbenzoic Isomers}	C ₉ H ₁₀ O ₂ Ethylbenzoic Isomers	C _{lo} H ₁₂ O ₂ Trimethylbenzoi Isomers
7-21	.50	1.6	1.4	1.0	.14	.005	.091	.019	_
7-9	.06	-	-	-	.0	.14	_	_	_
9-11	.47	1.3	2.5	.89	0	0	_	_	*-
11-13	.46	1.6	1.6	.64	.11	0	_	.025	.0050
13-15	.84	1.2	4.8	1.7	.36	_	_	_	_
15-17	.64	.97	2.7	2.0	.87	.57	_	_	_
17-19	.41	.64	.47	-	0	.76	_	_	-
19-21	.41	2.2	-	-	.12	-	-	_	-

	ne	ene		SECONDARY DIFUNCTIONALS								
TIME (PDT)	C ₅ H ₈ O ₃ Cyclohexene product?	C ₅ H ₁₀ O ₂ Cyclohexe product?	C ₅ H ₁₀₀₃ Isomers	C ₆ H _{8O2} 1-heptene product?	C ₆ H ₁₂ O ₃ Isomers	C ₇ H ₁₀ O ₂ Isomers	C ₇ H ₁₂ O ₂ Isomers	C ₇ H ₁₂ O ₃ Isomers	C ₈ H _{5O3} Phthalates			
7-21	.14	-	.067	.65	.041	.12	.14	.062	1.1			
7-9	-		~	.16	_	_	-	_	1.1			
9-11	-		1.4	1.2	.59	-	_	.096	2.0			
11-13	-	-	-	.88	_	.28	.27	_	2.0			
13-15	~	-	-	. 14		_	. 18	_	2.0			
15-17	-	-	-	-	.65	.58	_	_	.66			
17-19	-	-	.19	.23	-		_	_	1.9			
19-21	-	-,	.11	-	-	_	-	_	1.6			

		_		SECONDARY		CTIONALS		ROGEN
TIME (PDT)	C ₅ H ₇ NO ₄ HCO(CH ₂) ₃ COONO	C ₅ H ₇ NO ₅ HOOC(CH ₂) ₃ COONO	C ₅ H ₇ NO ₆ Isomers	C ₅ H ₉ NO ₄ HCO(CH ₂) ₄ ONO ₂ + Isomers	C ₅ H ₉ NO ₅ HOOC(CH ₂) ₄ ONO ₂	С ₆ Н9NO ₄ НСО(СН ₂) ₄ СООNО	C ₆ H ₉ NO ₅ HOOC(CH ₂) ₄ COONO	C6H9NO ₆ Isomers
7-21	•••	.018	-	.30	.026	-	_	~
7-9	.65		-	_	_	-	_	_
9-11	.12	-	-	-		_	_	_
11-13	-	-	-	_	_	_	_	_
13-15	.60		_	.42	.21	_	_	_
15-17	1.4	_	_	-	_	_	_	_
17-19	. 33	_	_	-	.15	_	-	_
19-21	.23	~	.13	~		-	- -	-

TIME (PDT)	C ₆ H ₁₁ NO _t HCO(CH ₂) ₅ ONO ₂ + Isomers	C ₆ H ₁ 1NO ₅ HOOC(CH ₂) ₅ ONO ₂	C ₂ H ₁₁ NO ₅ H00c(CH ₂) ₅ C00NO	C ₇ H ₁₃ NO _t HCO(CH ₂) ₆ ONO ₂ + Isomers	C ₇ H ₁ 3NO ₅ HOOC(CH ₂) ₆ ONO ₂ + Isomers ₆	ECONDARY DIFUNCTIONALS WITH NITROGEN (cont.)
7-21	.018	-	.031	_	_	
7-9	-	-	· -	_	_	
9-11	-		-	_		
11-13	-	-	-		-	,
13-15	-	-	_	-	_	
15-17	.16	-	-	_	_	
17-19	-	-	_	-	_	
19-21	-	-	-	_	-	

NITROGEN COMPOUNDS

CH ₂ CN Fragment (relative)	CONH Fragment (relative)	C ₃ H ₅ N ₂ Fragment (relative)	CH ₂ NO ₃ Fragment (relative)	C ₄ H ₈ N ₂ Fragment (relative)	C ₄ H ₉ N ₂ Fragment (relative)	C ₅ H ₅ N Pyridine & Pyridyls	C ₅ H ₁₀ N Piperidines + Isomers
.10	2.5	0	-		-	-	.010
.35	G	.7	.11	.04	.94	.026	.028
-	0	.47	-	.12	2.5	.030	.030
.22	2.5	.05	_	-	-	-	.015
2.6	0	.09	-	1.3	1.6	-	.056
1.7	3.8	.6	-	.23	.16	_	.097
4.1	0	.4	-	.26	.70	.11	-
1.4	5.2	.17	-	.86	1.1	.044	.089
	.10 .3522 .25	CH ₂ CN CN ₂ CN CNH CNH CNH CNH CNH CNH CNH CNH CNH C	CH ₂ CN CH ₂ CN CH ₂ CN CONH CH lativ CH lativ CONH CH lativ CONH CH lativ CH lativ C	CH ₂ CN CH ₂ CN CH ₂ CN CONH CREJATIV C	CH ² CN CH ² CN CH ² CN CH ² CN CH ² CN CH ² CN CH ² NO CH	CH2CN CH2CN CH2CN CH3CN CH3CN CH2CN CH	CH ² CN CH

NITROGEN COMPOUNDS (cont.)

TIME (PDT)	C ₇ H ₇ NO ₃ Hydroxynitro. toluene	C ₇ H ₇ NO ₄ Toluene oxidn. prod.	C ₉ H ₇ N Quinoline?	C ₁₀ H ₇ NO ₂ Nitro- naphthalene	C ₁₂ H ₉ N Carbazole	C ₁₃ H ₉ N Acridine + Isomers
7-21	.0028	-	.0034	-	.0085	-
7-9	-	0	-	-	_	
9-11	-	0	_	-	-	_
11-13	-	-	.0036	-	-	_
13-15	-	~	.032	-	_	
15-17	-	.003	.017	-	_	_
17-19	-	0	-	-		_
19-21	-	0	.028	_		-

	as acid	INORGA	NICS	CHLO	RINATED	COMPOUNDS	ہن
TIME (PDT)	Sulfates Sulfuric	Ammonium Chloride	Ammonium Nitrate	C ₁₂ H ₅ Cl ₃ PCB?	C ₇ H ₄ Cl ₃ Isodrin	C ₆ H ₄ Cl ₃ Lindane	C ₅ H ₅ Cl Heptachlor
7-21	6.6	.22	9.9	_	-	_	-
7-9	8.7	1.3	3.5	_	-	-	_
9-11	5.2	1.3	7.3	-	-	_	_
11-13	4.6	. 32	>20	-	-	_	•••
13-15	4.9	1.9	14.2	_	.20	-	_
15-17	2.6	1.0	1.3	_	.16	-	_
17-19	2.0	1.4	1.1	-	_	-	_
19-21	3.7	.62	.7	-	.092	-	-

TIME (PDT)	C ₉ H ₁₄ O ₂ Isomers	C ₁₀ H ₁₄ O ₃ Isomers	C ₁₀ H ₁₆ O ₂ Isomers	C ₁₀ H ₁₆ O ₃ (Pinonic Acid?)	TENTATIVE TERPENE PRODUCTS
7-21	.085	_	-	-	
7-9	-	-	_	-	
9-11	-	-	-	-	
11-13	.097	-	_	-	
13-15	-	-	_		
15-17	-	-	-	-	
17-19	-	-	-	-	
19-21	-	-	_	_	

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Pomona, California

		Μt	А	LIPHATIC	HYDROCA	RBONS		
TIME (PDT)	C ₅ H ₁₁ Total Alkanes	C ₆ H ₁₃ Alkanes, Low Molec	C ₆ H ₁₃ Alkanes, Med MW	C ₆ H ₁₃ Alkanes, High MW	C ₅ H ₉ Total Alkenes	C ₆ H ₁₁ Alkenes, Low MW	C ₆ H ₁₁ Alkenes, Med MW	C ₆ H ₁₁ Alkenes, High MW
7-21	.18	.029	.007	.026	.49	.020	.18	.11
7 - 9	.19	0	.10	.025	.49	.053	.12	.12
9-11	.13	0	.15	-	.74	.05	.30	.25
11-13	.05	0	.095	.081	.81	.056	.22	.16
13-15	.17	.005	.13	.010	.73	.046	.27	. 14
15-17	.21	0	.22	-	.92	.078	.25	.20
17-19	.32	.014	.12	.037	.85	.03	.29	.14
19-21	. 31	.006	.19	.014	.82	.006	.29	.25

es, Benzenes	ss, Benzenes	AROMA S	es	OCARBONS &
H7 len(kyl	10 en(y1	հյ Հջ] nzen	~~ U	Н ₁ 4 У1 zen
K X A J	C ₈ I	C ₉ F A1F Ber	CgF A1k Ben	C ₁₀ A1k Ben
.18	.091	.098	.035	.024
.17	.049	.061	.018	.019
.34	.10	.145	.091	.026
.29	.17	.175	. 11	.063
.30	.075	.126	.038	-
.35	.070	.175	.050	-
.26	.037	. 105	.085	.017
.30	-	. 128	.089	.036
	C ₇ H ₇ 81. C ₇ H ₇ 81. Xylenes, 10. 35. 35. 36. 36. 36. 36. 36. 36. 36. 36. 36. 36	C2H2 C2H4 C2H4 C2H4 C2H4 C2H4 C2H4 C2H4 C2H4 C2H4 C2H4 C2H4 C2H4 C2H4 C2H4 C2H4 C2H4 C2H4 C3H4	AROMA **Semanting** **AROMA **Semanting** **AROMA **Semanting** **AROMA **Semanting** **AROMA **Semanting** **AROMA **Semanting** **AROMA **ARO	AROMATIC HYDR AROMATIC HYDR AROMATIC HYDR Benzenes, and a service of the servi

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Pomona, California

		P	OLYCYC	LIC HYDR	COCARBONS	5	ene		
TIME (PDT)	C ₈ H ₈ Tetrahydro- nanhthalene	C ₉ H ₁₀ Indan	C ₁₀ H ₈ Naphthalene	C ₁₀ H ₁₈ Perhydro-	naphthalene C ₁₁ H ₁₀ Methyl-	naphthalenes C ₁₁ H ₁₃ Dimethyltetra-	hydronaphthal CluH10 Anthracene &	Phenanthrene C ₁₆ H ₁₀	Pyrene & Isomers
7-21	.082	-	.014	.050	.010	.00	69 -	. (0026
7-9	.085	-	.013	. 14	.044	.02	8 -		_
9-11	.21	-	.006	-	.010	.04	8 .00	46 .(38
11-13	.25	.0097	.035	-	_	.01	5 ~		BM
13-15	. 19	-		-	-	.05	9 -		-
15-17	.18	.068	.016	.052	_	.009	95 -		_
17-19	.10	.046	.005	1 .026	.007	6 .054	4 -		_
19-21	.044	.018	-	-	.022	.019	9 -		_
	(OXYGENAT	ED AROI	MATICS					
TIME (PDT)	C ₆ H ₄ O ₂ Benzoquinone?	C ₆ H ₅ O Phenol + NO ₂ ,CHO,COOH?	C ₆ H ₆ O Pheno1	C ₆ H ₆ O ₂ Dihydroxy- benzenes	C ₇ H ₆ O Benzaldehyde + Interference	C ₇ H ₈ O Hydroxytoluene + Benzyl Alcohol	C ₉ H ₁₂ O Trimethylphenol + Isomers	C ₁₂ H ₁₀ O ₂ Biphenol	C ₁₄ H ₂₁ O Dibutyl- methylphenol
7-21	-	-	.021	.047	-	.008	_	.040	.015
7-9	-	1.4	.019	.083	.039	.015	-	-	-
9-11	-	.44	.048	.12	.057	.072	.037	-	-
11-13	.014	. 36	.08	.12	-	.066	~	-	<u>-</u> ·
13-15	-	.19	.032	.081	-	.065	_	_	.033
15-17	-	.47	.067	.091	.038	.084	_	-	-
17-19	0	-	0	.072	-	.051	.054	.016	-
19-21	.033	.044	0	. 14	_	.018	.046	_	_

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Pomona, California

				oic	CARBOX	(YLIC AC	IDS		Ö
TIME (PDT)	C ₂ H ₄ O ₂ Total Acids (as acetic)	C ₄ H ₆ O ₂ Pentanedioic Acid	C ₅ H ₈ O ₂ Hexanedioic Acid	C ₆ H ₁₀ O ₂ Methylhexanedic Acid	C ₇ H ₅ O Benzoył Ion	C ₇ H ₆ O ₂ Benzoic Acid	C ₈ H _{8O2} Methylbenzoic Isomers	C ₉ H ₁₀ O ₂ Ethylbenzoic Isomers	C ₁₀ H ₁₂ O ₂ Trimethylbenzoi Isomers
7-21	.40	1.4	1.6	.49	.22	.044	.0099	.022	-
7-9	.37	.20	.34	. 34	0	0	.026	~	_
9-11	.72	4.1	1.5	.47	0	0	.081	.075	-
11-13	.68	3.5	3.5	1.5	0	0		.058	_
13-15	.58	4.4	3.4	.74	0	0	.029	-	-
15-17	.71	1.8	4.2	.97	0	0	.065	.032	.020
17-19	.82	2.6	2.9	1.8	.28	0	.018	.025	.016
19-21	.64	2.4	1.3	.88	.30	0	-	-	.069

€.

	SECONDARY DIFUNCTIONALS								
TIME (PDT)	C ₅ H ₈ O ₃ Cyclohexene product?	C ₅ H ₁₀ O ₂ Cyclohexene product?	C ₅ H ₁₀ O ₃ Isomers	C ₆ H _{8O2} 1-heptene product?	C ₆ H ₁₂ O ₃ Isomers	C7H ₁₀ O ₂ Isomers	C ₇ H ₁₂ O ₂ Isomers	C ₇ H ₁₂ O ₃ Isomers	C ₈ H ₅ O ₃ Phthalates
7-21	.074	-	***	.21	.048	. 35	.16	-	1.2
7-9	-	.076	.26	1.0	.10	. 34	-	_	1.4
9-11	-	-		1.1		1.1	-	.16	2.0
11-13	.81	.11	-	1.1	_	.22	. 34	.13	1.7
13-15	.13	-	_	.42	-	.22	.14	.16	1.3
15-17	.37	-	-	1.4	. 17	.71	. 38	-	1.4
17-19	.10	~~	_	1.2	-	.65	.48		2.0
19-21	-	_	-	.81	_	.37	-	.13	1.9

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Pomona, California

SECONDARY DIFUNCTIONALS WITH NITROGEN

TIME (PDT)	C ₅ H ₇ NO ₄ HCO(CH ₂) ₃ COONO	С ₅ H7NO ₅ H0OC(CH ₂) ₃ COONO	C ₅ H ₇ NO ₆ Isomers	C ₅ H ₉ NO ₄ HCO(CH ₂) ₄ ONO ₂ + Isomers	C ₅ H ₉ NO ₅ H00C(CH ₂) ₄ ONO ₂	С ₆ Н9NO ₄ HCO(СН ₂) ₄ СООNО	С ₆ Н ₉ NО ₅ НООС(СН ₂) ₄ СООNО	C ₆ H ₉ NO ₆ Isomers
7-21	_	-	-	-	.029	_		_
7-9	. 	-	_	-	•	_	.099	_
9-11	-	-	-		.23	-	_	_
11-13	-	-	.16	.23	-	-	_	-
13-15	-	.05	_	-	.12	_	_	_
15-17	-	.033	-	-	-		_	
17-19	-	-	-	.064	-	-		_
19-21	-		-	-	~	-	-	-
TIME (PDT)	C ₆ H ₁₁ NO ₄ HCO(CH ₂) ₅ ONO ₂ + Isomers	C ₆ H ₁₁ NO ₅ HOOC(CH ₂) ₅ ONO ₂	C ₇ H ₁₁ NO ₅ HOOC(CH ₂) ₅ COONO	C ₇ H ₁₃ NO ₄ HCO(CH ₂) ₆ ONO ₂ + Isomers	C ₇ H ₁ 3NO ₅ HOOC(CH ₂) ₆ ONO ₂ + Isomers		ARY DIFU ITROGEN	NCTIONALS (cont.)
7-21	.045	.042	-	.082	.018			
7-9	-	-	~	-	-			
9-11	-	-	-	~	-			
11-13		-	-	-	-			
13-15	-		-	-	-			
15-17	-	-	-		-			
17-19	.054	_	_	-	_			

19-21

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Pomona, California

NITROGEN COMPOUNDS

TIME (PDT)	CH ₂ CN fragment (relative)	CONH fragment (relative)	C ₃ H ₅ N ₂ fragment (relative)	CH ₂ NO ₃ fragment (relative)	C ₄ H ₈ N ₂ fragment (relative)	C ₄ H ₉ N ₂ fragment (relative)	C _{SHS} N Pyridine & Pyridyls	C ₅ H ₁₀ N Piperidined & Isomers
7-21	.18	2.2	0	_	_	.024	.0037	.0098
7-9	-	1.7	-	~	_	_	_	_
9-11	.44	4.3	.22	-	•	.11	.0082	.038
11-13	-	1.4	.07	_	.77	-	-	.070
13-15	.61	3.6	0	_	1.4	. 30	_	.070
15-17	.14	2.5	_		_	_	.0069	.059
17-19	.49	3.1	0		_		-	.037
19-21	. 14	3.0	.10	-	-	.13	_	.018

NITROGEN COMPOUNDS (cont.)

TIME (PDT)	C ₇ H ₇ NO ₃ Hydroxynitro. toluene	C ₇ H ₇ NO ₄ Toluene oxidn. prod.	C ₉ H ₇ N Quinoline?	C ₁₀ H7NO ₂ Nitro- naphthalene	C ₁₂ H ₉ N Carbazole	C ₁₃ H ₉ N Acridine & Isomers
7-21	-	-	.0035	.0017	.012	_
7-9				-	-	-
9-11	-	0	.0084	_	_	_
11-13	-	-	-	_	.0055	
13-15	-	_	_	_	_	_
15-17	-	.003	.045	_	_	_
17-19	-	-	.041		.011	_
19-21		-	_	_	_	.015

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Pomona, California

	p	INORGAN	ICS	CHLOR	INATED	COMPOUNDS		
TIME (PDT)	Sulfates as Sulfuric Ac	Ammonium Chloride	Ammonium Nitrate	C ₁₂ H ₅ CI ₃ PCB?	C ₇ H ₄ Cl ₃ Isodrin	C ₆ H ₄ Cl ₃ Lindane	C _S H ₅ Cl Heptachlor?	
7-21	6.0	>.53	11.	_	-	.026	-	
7-9	8.2	.65	1.7	-	-	0	0	
9-11	11.7	4.0	32		-	.47	0	
11-13	2.9	2.2	4.8	-	_	0	0	
13-15	3.6	1.5	3.3	_	_	0	0	
15-17	4.0	1.1	2.4		_	0	0	
17- 19	4.9	1.2	3.5	-	_	_	-	
19-21	6.2	1.0	4.5	<u>-</u>	-	0	0	

TENTATIVE TERPENE PRODUCTS

TIME (PDT)	C ₉ H ₁₄ O ₂ Isomers	C ₁₀ H ₁₄ O ₃ Isomers	C ₁₀ H ₁₆ O ₂ Isomers	C _{lo} H _{l6} O ₃ Pinon <u>i</u> c Acid?
7-21	.034	.045	_	-
7-9	-	.32	-	-
9-11	-	-	.12	-
11-13		-	_	-
13-15	•	-	~	-
15-17	. 35	· _	-	_
17-19	.20	_	_	-
19-21	-	-	-	-

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Riverside, California

TIME (PDT)	C ₅ H ₁₁ Total Alkanes	C ₆ H ₁₃ Alkanes, Low Molec	C ₆ H ₁₃ Alkanes, Med MW	C ₆ H ₁₃ Alkanes, High MW	C ₅ H ₉ Total Alkenes	C ₆ H ₁₁ Alkenes, Low MW	C ₆ H ₁₁ Alkenes, Med MW	C ₆ H ₁₁ Alkenes, High MW		
7-21	.06	0	.034	.022	.22	_	.068	.088		
7-9	.13	.02	.04	.01	.39	.02	. 11	.09		
9-11	.25	.046	.14	.06	.53	.04	.25	.16		
11-13	.11	.013	.047	-	.46	.055	.08	.076		
13-15	.45	.08	.068	.09	1.04	.059	. 19	.51		
15-17	.15	.031	.077	.0050	.51	.040	. 16	.072		
17-19	.07	0	.015	-	.56	.024	.077	.10		
19-21	.49	.08	.26	.036	.95	.083	.32	.36		

TIME (PDT)	C ₇ H ₇ Xylenes, Alkyl Benzenes	C ₈ H ₁₀ Xylenes, Ethyl Benzenes	C ₉ H ₁₁ A1kyl Benzenes D	C ₉ H ₁₂ Alkyl Benzenes H	C ₁₀ H ₁₄ Alkyl Benzenes go	18
7-21	.09	.018	.037	.0040		
7-9	.17	0	.093	-	_	
9-11	.20	.02	.093	.077	.011	
11-13	.21	0	.060	.030	.18	
13-15	.55	.017	.005	.025	-	
15-17	.09	0	.057	.0038	_	
17-19	.10	-	0	_	_	
19-21	.50	.14	.193	.035	-	

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Riverside, California

POLYCYCLIC HYDROCARBONS										
TIME (PDT)	C ₈ H ₈ Tetrahydro- naphthalene	C ₉ H ₁₀ Indan	C ₁₀ H ₈ Naphthalene	CloH18 Perhydro-	naphtnalene C ₁₁ H ₁₀ Methyl- naphthalenes	C ₁₁ H ₁₃ Dimethyltetra- hvdronaphthalene	$C_{14}H_{10}$ Anthracene &	CleH10		
7-21	.050	.0040	.0063	-	स र	,014	-	_		
7-9	.061	.0057	.003	-	-	.010	_	•••		
9-11	.18	.024	.031	-	.025	Ġ	_	.00	69	
11-13	.12	.026	.005	-	_	-	_		03	
13-15	-	.020	-	,067	-	-	-	_		
15-17	,096	.0048	.015		_	.0030	_	_		
17-19	-	.010	7	-	•••	_	_	_		
19-21	, 15	.049	.022	inet	-	.022	-	_		
		OXYGENA	TED ARC	MATICS		+				
TIME (PDT)	C ₆ H ₄ O ₂ Benzoquinone?	C ₆ H ₅ O Phenol + NO ₂ ,CHO,COOH?	C ₆ H ₆ O Pheno1	C ₆ H ₆ O ₂ Dihydroxy - benzenes	C ₇ H ₆ O Benzaldehyde + Interference	С ₇ Н ₈ О Hydroxytoluene ч Benzyl Alcohol	C ₉ H ₁₂ O Trimethylphenol + Isomers	C ₁₂ H ₁₀ O ₂ Biphenol	C _{lu} H ₂₁ O Dibutyl- methylphenol	
7-21	_	.040	.014	.040	.0052	.024	_	_	_	
7-9	-	.106	.016	.027	-	.027	.011	_		
9-11	-	.29	.086	.072	.0003	.034		.010	.012	
11-13	-	.37	.016	.037	.013	.033		_	.027	
13-15	.014	.24	.09	.10	-	.051		.061	_	
15-17	-	.29	.07	.063	.0044	.042		.0075	_	
17-19	-	.20	0	.027		-	.043	_	_	
19-21	.027	.50	.16	.077	0	.091	.035	_	.10	
									-	

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Riverside, California

				ioic	CARBOXYLIC ACIDS							
TIME (PDT)	C ₂ H ₄ O ₂ Total Acids (as acetic)	C ₄ H ₆ O ₂ Pentanedioic Acid	C ₅ H ₈ O ₂ Hexanedioic Acid	C ₆ H ₁₀ O ₂ Methylhexanedic Acid	C ₇ H ₅ O Benzoy1 Ion	C ₇ H ₆ O ₂ Benzoic Acid	C ₈ H ₈ O ₂ Methylbenzoic Isomers	C ₉ H ₁₀ O ₂ Ethylbenzoic Isomers	C ₁₀ H ₁₂ O ₂ Trimethylbenzoi Isomers			
7-21	.27	.84	.88	.40	0	0	.0082	~	_			
7-9	.26	.29	1.0	.55	0	0	-	_	_			
9-11	.68	1.9	1.9	.62	0	0	.043	.029	-			
11-13	.71	3.0	3.8	1.1	.1	0	.030	_	_			
13-15	.92	2.1	3.0	.46	.9	.13	_	_	_			
15-17	.82	1.7	1.4	1.2	.15	0	_	.016				
17-19	.23	.96	1.0	-	0	0		~	_			
19-21	1,0	2.9	3.4	.44	0	0	.038	-	_			

	ဥ္ SECONDARY DIFUNCTIONALS									
TIME (PDT)	C ₅ H ₈ O ₃ Cyclohexene product?	C ₅ H ₁₀ O ₂ Cyclohexene product?	C ₅ H ₁₀ O ₃ Isomers	C ₆ H ₈ O ₂ 1-heptene product?	C ₆ H ₁₂ O ₃ Isomers	C ₇ H ₁₀ O ₂ Isomers	C ₇ H ₁₂ O ₂ Isomers	C ₇ H ₁₂ O ₃ Isomers	C ₈ H ₅ O ₃ Phthalates	
7-21	-	-	.060	.49	_	.10	-	.075	.43	
7-9	-		-	.53	-	.040	.036	_	.96	
9-11	.086	-	.090	.87	_	.30		_	1.5	
11-13	.10	-	.17	.85	_	.67	.087	. 14	1.9	
13-15	.18		_	. 20	-	. 15	_	_	1.9	
15-17	.037		-	.76	_	.42	.13	-	1.5	
17-19	-	~	-	. 14	_	-	_	_	.80	
19-21	-	-	-	1.1	-	.66	.092	•••	2.5	

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Riverside, California

SECONDARY DIFUNCTIONALS WITH NITROGEN

TIME (PDT)	C ₅ H ₇ NO ₄ HCO(CH ₂) ₃ COONO	С ₅ H ₇ NO ₅ HOOC(CH ₂) ₃ COONO	C ₅ H ₇ NO ₆ Isomers	C ₅ H ₉ NO ₄ HCO(CH ₂) ₄ ONO ₂ + Isomers	C ₅ H ₉ NO ₅ HOOC(CH ₂) ₄ ONO ₂	C ₆ H ₉ NO ₄ HCO(CH ₂) ₄ COONO	С ₆ Н ₉ NО ₅ НООС (СН ₂) ₄ СООNО	C ₆ H ₉ NO ₆ Isomers
7-21	-	_	_	.13	_	_	Ξ.	
7-9	.040	-	_	_	_	_	_	
9-11	_	-		.052	_	_	-	-
11-13		-	_	-	16	_	-	-
13-15			_		.16	_	-	~
15-17	-	_	_	.059	.021	-	~	•
17-19	_	_	_	-	.021	_	-	-
19-21	_	_	_	. 14	.07	-	-	-
TIME (PDT)	C ₆ H ₁₁ NO ₄ HCO(CH ₂) ₅ ONO ₂ + Isomers	C ₆ H ₁₁ NO ₅ H00C(CH ₂) ₅ ONO ₂	C ₇ H ₁ NO ₅ HQGC(CH ₂) ₅ COONO	С ₇ Н ₁₃ NO ₄ НСО(СН ₂) ₆ ONO ₂ + Isomers	C ₇ H ₁ 3NO ₅ HOOC(CH ₂) ₆ ONO ₂ + Isomers	SECONDAF	RY DIFUN FROGEN (CTIONALS cont.)
7-21	-	-	-	.035	-			
7-9	-	-	-	.040	-			
9-11	.10	-	-	_	-			
11-13	-	-	-	-	_			
13-15	~	-	_	_	-			
15-17	-	.026	-	-	_			
17-19	-	-	-	-	_			
19-21	.22	_	_	-	-			

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Riverside, California

NITROGEN COMPOUNDS

TIME (PDT)	CH ₂ CN fragment (relative)	CONH fragment (relative)	C ₃ H ₅ N ₂ fragment (relative)	CH ₂ NO ₃ fragment (relative)	C ₄ H _{8N2} fragment (relative)	C ₄ H ₉ N ₂ fragment (relative)	C ₅ H ₅ N Pyridine & Pyridyls	C _S H ₁₀ N Piperidines & Isomers
7-21	.14	2.2	0	-	_		_	.0037
7-9		2.0	-	-		.058	.0018	_
9-11	.32	3.0	0	-	-	.12		.0071
11-13	. 39	4.2	.4	-	_	.38	.17	.19
13-15	.96	9.3	-		_	_	_	-
15-17	.34	4.2	_		_	_		_
17-19	.19	2.7	.25	_	_	_	_	<i>-</i>
19-21	.48	6.9	0	.075	-	.10	.041	.052

NI IGGEN COMPOUNDS (cont.)

TIME (PDT)	C ₇ H ₇ NO ₃ Hydroxynitro toluene	C ₇ H ₇ NO ₄ Toluene oxidn. prod.	C ₉ H ₇ N Quinoline?	C _{lo} H ₇ NO ₂ Nitro- naphthalene	C ₁₂ H ₉ N Carbazole	C ₁₃ H ₉ N Acridine & Isomers
7-21	-	_	.0040	_		_
7-9	_	-	_	_	_	_
9-11	-	-	-	_	_	_
11-13	-	.009	.0068		_	-
13-15		~	.026	-	_	_
15-17	-	~	_		_	_
17-19	~	_	.012	-	-	_
19-21	-	-	.025	-	_	.023

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 9, 1975, at Riverside, California

	٦	INORGA	NICS	CHLORINATED COMPOUNDS					
TIME (PDT)	Sulfates as Sulfuric Aci	Ammonium Chloride	Ammonium Nitrate	C ₁₂ H ₅ C1 ₃ PCB?	C ₇ H ₄ Cl ₃ Isodrin	C ₆ H ₄ Cl ₃ Lindane	C _S H _S Cl Heptachlor?		
7-21	1.7	. 35	>15	.017	_	-	_		
7-9	4.8	1.9	9.5	-	~	-	0		
9-11	5.0	3.2	>40	-	-	0	_		
11-13	4.9	2.6	24.	-	-	_	_		
13-15	4.3	1.8	>30	-	_	0	0		
15-17	3.5	.40	1.8	-	-	•••	_		
17-19	2.5	1.5	11.7	-	-	0	_		
19-21	7.1	3.2	>40.	-	-	0	0		

TENTATIVE TERPENE PRODUCTS

TIME (PDT)	C ₉ H ₁₄ O ₂ Isomers	C ₁₀ H ₁₄ O ₃ Isomers	C ₁₀ H ₁₆ O ₂ Isomers	C ₁₀ H ₁₆ O ₃ Pinonic Acid?
7-21	_	_	-	_
7-9	-	-	-	_
9-11	_	.026	-	-
11-13	-	-	_	-
13-15	-	-	-	-
15-17	_	-	_	-
17-19	-	-	-	-
19-21	•••	. 12		-

		Σ	A	ALIPHATIC	HYDROCA	ARBONS		
TIME (PDT)	C ₅ H ₁₁ Total Alkanes	C ₆ H ₁₃ Alkanes, Low Molec	C ₆ H ₁₃ Alkanes, Med MW	C ₆ H ₁₃ Alkanes, High MW	C ₅ H ₉ Total Alkenes	C ₆ H ₁₁ Alkenes, Low MW	C ₆ H ₁₁ Alkenes, Med MW	C ₆ H ₁₁ Alkenes, High MW
7-21	.14	.008	.083	.039	.38	_	.096	.16
7-9	.14	.03	.08	.03	.49	0	.21	.10
9-11	.16	.04	.05	.003	.57	.06	.11	.09
11-13	.29	.07	.05	.006	.77	.07	.22	.15
13-15	.31	.01	.12	.027	.86	0	.32	.19
15-17	.17	.05	.026	-	.53	.02	.19	.09
17-19	.20	.04	.07	.01	.49	.027	.21	.09
19-21	.22	.06	.04	-	.43	.056	.16	.07

	nzenes	zenes	AR	OMATIC H	YDROCARI	BONS
TIME (PDT)	C ₇ H ₇ Xylenes, Yakyl Ber	C ₈ H ₁₀ Xylenes, Alkyl Ben	C ₉ H ₁₁ A1kyl Benzenes	C ₉ H ₁₂ Alkyl Benzenes	C ₁₀ H ₁₄ Alkyl Benzenes	C ₁₂ H ₁₀ Biphenyl
7-21	.16	.066	.095	.066	.056	_
7-9	.19	.02	.007	-	-	.0035
9-11	.21	.003	.065	-	.020	_
11-13	.27	.07	.096	.029	.011	_
13-15	.27	.15	.131	.089	.024	~
15-17	.18	.023	.004	.017	-	~
17-19	.15	.004	.021	.0061		-
19-21	.12	•••	.049	.0090	-	

			POLYCYCLIC	HYDROCA	RBONS	ene		
TIME (PDT)	C ₈ H ₈ Tetrahydro- naphthalene	C ₉ H ₁₀ Indan	.C ₁₀ H ₈ Naphthalene	C ₁₀ H ₁₈ Perhydro- naphthalene	C ₁₁ H ₁₀ Methyl- naphthalenes	C ₁₁ H ₁₃ Dimethyltetra hydronaphthal	C ₁₄ H ₁₀ Anthracene & Phenanthrene	C ₁₆ H ₁₀ Pyrene & Isomers
7-21	.078	.036	.015	.015	.0045	.025	-	-
7-9	.083	-	-	-	.020	.0083	-	_
9-11	.087	.024	.022	-	_	_	~	-
11-13	.083	.021	.025	_	.0068	.064	_	_
13-15	.078	.019	_	.018	.0061	.049	_	_
15-17	.071	.010	.0036	_	-	.0090	~	
17~19	.025	.012	.0015	_		.0054		_
19-21	.047	-	.004	-	-	.0070	-	· _
			(DXYGENAT	ED AROMA	TICS		

TIME (PDT)	C ₆ H ₄ O ₂ Benzoquinone?	С ₆ Н ₅ О Phenol + NO ₂ ,СНО,СООН?	C ₆ H ₆ O Phenol	C ₆ H ₆ O ₂ Dihydroxy- benzenes	C ₇ H ₆ O Benzaldehyde + Interference	C ₇ H ₈ O Hydroxytoluene + Benzyl Alcohol	C ₉ H ₁₂ O Trimethylphenol + Isomers	C ₁₂ H ₁₀ O ₂ Biphenol	C ₁₄ H ₂₁ O Dibutyl- methylphenol
7-21	.0032	.050	.011	.095	.017	.026	.028	.0059	.010
7-9	-	~	.006	.094	.006	.023	.013	-	-
9-11	-	-	.025	.134	-	.066	-	_	_
11-13	-	.046	.037	.094	.028	.055	.019	-	_
13-15	-	.024	.09	.124		.048	.16	.0091	.016
15-17	_	-	.01	.042	-	.05	.047	_	_
17-19	.0087	-	.008	.019	.0089	.016	.044	_	-
19-21	-	. 19	.006	.052	0	0	.018		

				oic	CARBO	XYLIC AC	IDS		jc
TIME (PDT)	C ₂ H ₄ O ₂ Total Acids (as acetic)	C _t H ₆ O ₂ Pentanedioic Acid	C ₅ H ₈ O ₂ Hexanedioic Acid	C ₆ H ₁₀ O ₂ Methylhexanedio Acid	C ₇ H ₅ O Benzoyl Ion	C ₇ H ₆ O ₂ Benzoic Acid	C ₈ H ₈ O ₂ Methylbenzoic Isomers	C ₉ H ₁₀ O ₂ Ethylbenzoic Isomers	benzo
7-21	.51	1.3	1.8	. 94	. 14	.02	.022	.041	~
7-9	1.4	2.6	1.2	1.1	.22	0	-	-	
9-11	1.3	2.0	2.2	1.2	.28	-	.016	-	.012
11-13	.88	1.9	2.9	1.2	.28	0	.028	-	_
13-15	.65	2.8	3.4	2.2	.21	0	.055	.024	_
15-17	.41	2.0	1.3	1.0	.19	_	_	.017	-
17-19	.37	1.5	1.1	.55	.11	-	-	_	-
19-21	.29	.97	.94	.48	0	0	-	-	-

	<u>ə</u>	<u>ə</u>	SEC	ONDARY DI	FUNCTIO	NALS			
TIME (PDT)	C ₅ H ₈ O ₃ Cyclohexene product?	C ₅ H ₁₀ O ₂ Cyclohexene product?	C ₅ H ₁₀ O ₃ Isomers	C ₆ H ₈ O ₂ 1-heptene product?	C ₆ H ₁₂ O ₃ Isomers	C ₇ H ₁₀ O ₂ Isomers	C ₇ H ₁₂ O ₂ Isomers	C ₇ H ₁₂ O ₃ Isomers	C ₈ H _{5O3} Phthalates
7-21	.018	.12	.077	.62	-	.31	.24	.025	.74
7-9	.060	-	-	.71	_	-	-	_	2.2
9-11	-	-	~	.77	-	.72	.12	-	1.8
11-13	.23	.078	-	.73	-	.54	.44	-	2.1
13-15	.20	-	-	1.3	.084	.74	.23	.062	1.5
15-17		_	-	.38	~	.45	.32		1.5
17-19	.048	-	-	.79	-	-	_	_	1.8
19-21	-	-	-	,65	-	.17	-	-	2.3

SECONDARY DIFUNCTIONALS WITH NITROGEN

TIME (PDT)	C ₅ H ₇ NO ₄ HCO(CH ₂) ₃ COONO	C ₅ H ₇ NO ₅ HOOC(CH ₂) ₃ COONO	C ₅ H ₇ NO ₆ Isomers	C ₅ H ₉ NO ₄ HCO(CH ₂) ₄ ONO ₂ + Isomers	C ₅ H ₉ NO ₅ HOOC(CH ₂) ₄ ONO ₂	C ₆ H ₉ NO ₄ HCO(CH ₂) ₄ COONO	С ₆ Н ₉ NО ₅ HOOC(CH ²) ⁴ COONO	C ₆ H ₉ NO ₆ Isomers
7-21	-	-	-	.031	-	-	.044	_
7-9	-	-	.073	.15	_	_	_	-
9-11	-	-		.053	.008	_	_	_
11-13	-	-	=	.061	.06	-	_	_
13-15	-		-	-	_	_	-	_
15-17	-	-	_	_	-		_	_
17-1 9	-	-	_	~	0	-	-	_
19-21	-	-	-	.048	-	-	-	-

TIME (PDT)	C ₆ H ₁ NO ₄ HCO(CH ₂) ₅ ONO ₂ + Isomers	C ₆ H ₁ NO ₅ HOOC(CH ₂) ₅ ONO ₂	C ₇ H ₁₁ NO ₅ HOOC(CH ₂) ₅ COONO	C ₇ H ₁₃ NO _t HCO(CH ₂) ₆ ONO ₂ + Isomers	C ₇ H ₁₃ NO ₅ HOOC(CH ₂) ₆ ONO ₂ + Isomers	SECONDARY DIFUNCTIONALS WITH NITROGEN (cont.)
7-21	.020	-	.046	.025	-	
7- 9	-	.073	-	.068	_	
9-11		-	- ,	_	_	
11-13	-	, - ,	-	.048	-	•
13-15	-	~		**	-	
15-17	-	-	_	-	-	
17-19	-	-	_	. 10	-	
19-21	•	-	-	**		•

NITROGEN COMPOUNDS

TIME (PDT)	CH ₂ CN fragment (relative)	CONH fragment (relative)	C ₃ H ₅ N ₂ fragment (relative)	CH ₂ NO ₃ fragment (relative)	C ₄ H ₈ N ₂ fragment (relative)	C ₄ H _{9N2} fragment (relative)	C ₅ H ₅ N Pyridine & Pyridyls	C ₅ H ₁₀ N Piperidines & Isomers
7-21	.11	1.8	-	-	_	.057	_	_
7-9	.21	1.9	0	-	_	~	_	.025
9-11	.092	1.4	-	028	_	_	_	.050
11-13	.052	2.2	~	-	-	-		.025
13-15	.26	1.5	0	_		_	_	.0053
15-17	-	. 39	0	-	-	_	_	.0062
17-19	-	.8	-	_	_	.065	_	-
19-21	.092	.7	0	-	-	-	-	.030

NITROGEN COMPOUNDS (cont.)

TIME (PDT)	C ₇ H ₇ NO ₃ Hydroxynitro toluene	C ₇ H ₇ NO ₄ Toluene oxidn. prod.	C ₉ H ₇ N Quinoline?	C ₁₀ H7NO ₂ Nitro- naphthalene	C ₁₂ HgN Carbazole	C ₁₃ H ₉ N Acridine & Isomers
7-21	.0062	-	.0030	-	.0079	_
7-9	-	-	-	.0023	_	_
9-11	, –	-	-	_	.0022	_
11-13	-	-	.013	-	_	_
13-15	~	-	.0029	-	.014	-
15-17	-	_	.014	-	_	•••
17-19	-	~	~	-	_	-
19-21	~	-	.0056		_	-

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 10, 1975, at Pasadena (Caltech)

	.;.	INORGA	NICS	CHLO	RINATED	COMPOU	
TIME (PDT)	Sulfates as Sulfuric Ac	Ammonium Chloride	Ammonium Nitrate	C ₁₂ H ₅ Cl ₃ PCB?	C ₇ H ₄ Cl ₃ Isodrin	C ₆ H ₄ Cl ₃ Lindane	C _S H ₅ Cl Heptachlor?
7-21	4.8	.01	5.5	-	-	0	-
7-9	6.0	.31	1.2	-	-	-	0
9-11	3.7	.87	4.6	_	-	-	
11-13	3.0	.51	>15	-	_	-	-
13-15	2.9	1.3	5.3	-	-	-	0
15-17	1.9	.27	.6	-	_	-	-
17-19	2.1	.31	.6	-	· _	_	-
19-21	2.2	.56	.6	-	-	-	0

TENTATIVE TERPENE PRODUCTS

TIME (PDT)	C ₉ H ₁₄ O ₂ Isomers	C ₁₀ H ₁₄ O ₃ Isomers	C ₁₀ H ₁₆ O ₂ Isomers	C ₁₀ H ₁₆ O ₃ Pinonic Acid?
7-21	.093	.020	-	~
7-9	.11	_	-	_
9-11	.057	-	-	
11-13	. 14	-	-	_
13-15	.044	-	.062	-
15-17		~	-	-
17-19	-	-	-	-
19-21	-	_	_	_

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 10, 1975, at Pomona, California

		c ≅	AL	IPHATIC	HYDROCAR	BONS		
TIME (PDT)	C ₅ H ₁₁ Total Alkanes	C ₆ H ₁₃ Alkanes, Low Molec	C ₆ H ₁₃ Alkanes, Med MW	C ₆ H ₁₃ Alkanes, High MW	C ₅ H ₉ Total Alkenes	C ₆ H ₁₁ Alkenes, Low MW	C ₆ H ₁₁ Alkenes, Med MW	C ₆ H ₁₁ Alkenes, High MW
7-21	.18	.019	.070	.018	.41	0	.16	.11
7-9	.38	.03	.18	.048	1.04	.15	.26	.16
9-11	.22	.014	.066	.036	.83	.13	.20	.17
11-13	.26	.09	.12	.014	.62	.085	.16	.22
13-15	.37	.034	.18	.027	.69	0	.31	.17
15-17	.50	.06	.15	.033	.94	.10	.42	.11
17-19	.53	.19	.13	.027	1.04	.10	.28	.12
19-21	.83	0	-	.34	.94	.04	.012	.51

TIME (PDT)	C ₇ H ₇ Xylenes, Alkyl Benzenes	C ₈ H ₁₀ Xylenes, Ethyl Benzenes	C ₉ H ₁₁ A1kyl Benzenes	C ₉ H ₁₂ A1kyl Benzen es	C ₁₀ H ₁₄ A1kyl Benzenes	C ₁₂ H ₁₀ SS Biphenyl	C ₁₃ H ₁₂ Diphenylmethane & Isomers
7-21	.18	.049	.070	.015	.023	-	-
7-9	.58	.12	.298	.057	.068	.0092	_
9-11	.43	.044	.210	.038	.040	_	
11-13	.40	.29	.058	.014	.024	_	_
13-15	. 17	.066	.086	.034	-	_	-
15-17	.43	.065	.193	.10	-	-	-
17-19	.42	.22	.263	.069	-	_	.016
19-21	.32	.058	.175	.020	.032	-	_

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 10, 1975, at Pomona, California

		POL	YCYCLI	C HYDROCA		ene			
TIME (PDT)	C ₈ H ₈ Tetrahydro- naphthalene	C ₉ H ₁₀ Indan	C _{lo} H ₈ Naphthalene	C ₁₀ H ₁₈ Perhydro- naphthalene	C ₁₁ H ₁₀ Methyl- naphthalenes	C _{llHl3} Dimethyltetra- hydronaphthalene	C ₁₄ H ₁₀ Anthracene & Phenanthrene	CleHlo &	Isomers
7-21	.010	.0057	.0014	_	-	.018	_	.00	41
7-9	.22	.18	.052	.11	.017	.13	.0079	-	
9-11	.13	.093	.0070	-	.0077	.019	_	.04	4
11-13	.10	.038	.051	-	-	.016	-	_	
13-15	.049	.010	.017	-	-	.031	~	-	
15-17	.30	.10	.076	.24	_	.076	-	-	
17-19	. 17	.053	.014	-	.022	.036	-	-	
19-21	.24	.040	.013	.15	-	.033	-	_	
			NTED AR	COMATICS	<u>.</u>	+	<u></u>		
TIME (PDT)	C ₆ H ₄ O ₂ Benzoquinone?	C ₆ H ₅ O Phenol + NO ₂ ,CHO,COOH?	C ₆ H ₆ O Pheno1	C ₆ H ₆ O ₂ Dihydroxy- benzenes	C ₇ H ₆ O Benzaldehyde + Interference	C ₇ H ₈ O Hydroxytoluene - Benzyl Alcohol	C ₉ H ₁₂ O Trimethylphenol + Isomers	C ₁₂ H ₁₀ O ₂ Biphenol	C _{lu} H ₂₁ O Dibutyl- methylphenol
7-21	_	-	.023	.045	-	.030	O ⊢ +	.0040	ODE
7-9	.022	.38	.04	.20	.061	.16	.079	-	_
9-11	-	.19	.04	. 17	.017	.13	.19	.086	_
11-13	.028	.36	.07	.11	.012	.043	.029	-	~
13-15	_	.003	.005	.052	_	.032	.017	_	.019
15-17	-	_	.089	.16	.044	.070		_	-
17- 19	-	.44	.11	.21	.25	.052	_	-	.021
19-21	-	.42	.10	.19	.15	.10	.10	.029	_

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 10, 1975, at Pomona, California

				ioic	CARBOXY	LIC ACID)\$		ာ
TIME (PDT)	C ₂ H ₄ O ₂ Total Acids (as acetic)	C ₄ H ₆ O ₂ Pentanedioic Acid	C ₅ H ₈ O ₂ Hexanedioic Acid	C ₆ H ₁₀ O ₂ Methylhexanedioic Acid	C ₇ H ₅ O Benzoyl Ion	C ₇ H ₆ O ₂ Benzoic Acid	C ₈ H ₈ O ₂ Methylbenzoic Isomers	C ₉ H ₁₀ O ₂ Ethylbenzoic Isomers	C ₁₀ H ₁₂ O ₂ Trimethylbenzo Isomers
7-21	.32	1.4	1.1	.64	.09	0		.0084	_
7-9	.82	4.0	4,3	2.0	0	0	.	.062	_
9-11	.76	4.1	3,6	2,2	,81	. 07	-	-002	.042
11-13	,56	2.0	1,7	1.4	0	0	-		.042
13-15	,56	1.4	2.0	.91	,07	0	_	_	~
15-17	2.9	3,0	2,3	,52	,61	.005		-	-
17-19	1,2	5.9	4.7	.71	2.5	, 4	_	- 075	.096
19-21	,49	.73	1.9	.52	2.1	, , 6	, 053	.075 .038	-

	пе	ene	SEC	ONDARY DI	FUNCTIO	NALS			
TIME (PDT)	C ₅ H ₈ O ₃ Cyclohexene product?	C ₅ H ₁₀ O ₂ Cyclohexel product?	C ₅ H ₁₀ O ₃ Isomers	C ₆ H ₈ O ₂ 1-heptene product?	C ₆ H ₁₂ O ₃ Isomers	C ₇ H ₁₀ O ₂ Isomers	C ₇ H ₁₂ O ₂ Isomers	C ₇ H ₁₂ O ₃ Isomers	C ₈ H ₅ O ₃ Phthalates
7-21	-	-	-	.55	-	. 34	_	.072	.46
7-9	. 39	-	.59	3.3	.28	2.4	.48	_	1.3
9-11	-	-	-	1.8	.11	1.2	.21	.31	1.4
11-13	. 14	-	.13	.90	~	.27	_		1.3
13-15	-	.076	-	_	.091	.54	.27	_	2.8
15-17	.18	-	~	.64	.13	.86	_	-	3.3
17-19	.76	-	.14	2.0	.31	t	_	_	
19-21	.16	.094	.44	1.0	-	. 14	. 14	- -	3.1 2.0

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 10, 1975, at Pomona, California

SECONDARY DIFUNCTIONALS WITH NITROGEN

					511 01	ioi Ional	-2 MIIII	MIIKOGEN
TIME (PDT)	C ₅ H ₇ NO ₄ HCO(CH ₂) ₃ COONO	С ₅ H ₇ NO ₅ HOOC(CH ₂) ₃ COONO	C ₅ H ₇ NO ₆ Isomers	C ₅ H ₉ NO ₄ HCO(CH ₂) ₄ ONO ₂ + Isomers	C ₅ H ₉ NO ₅ HOOC(CH ₂) ₄ ONO ₂	C ₆ H ₉ NO ₄ HCO(CH ₂) ₄ COONO	C ₆ H ₉ NO ₅ HOOC(CH ₂) ₄ COONO	C ₆ H ₉ NO ₆ Isomers
7-21	.029	-	-	-	_	-	_	_
7-9	.093	-	.083	-	.12		.12	_
9-11	-	-	. 10		.19	_	_	_
11-13		-	-	.18	_		_	_
13-15		-	.071	_	_	_	_	-
15-17	-	-	_	_	_	_	,	-
17-19	_	_	-	-	_	_	~	-
19-21	-	_	. 16	_	_	_	-	-
						-	-	-

TIME (PDT)	C ₆ H ₁ NO ₄ HCO(CH ₂) ₅ ONO ₂ + Isomers	C ₆ H ₁ 1NO ₅ H0OC(CH ₂) ₅ ONO ₂	C ₇ H ₁₁ NO ₅ HOOC(CH ₂) ₅ COONO	C ₇ H ₁₃ NO ₄ HCO(CH ₂) ₆ ONO ₂ + Isomers	C ₂ H ₁₃ NO ₅ HOOC(CH ₂) ₆ ONO ₅ + Isomers + Isomers + Cont.)
7-21	.061	-	_	_	_
7-9	-	-	~	_	_
9-11	-	-	-	_	~
11-13	-	_	_	_	_
13-15	•••	-	_	_	_
15-17	_	-		_	_
17-19	.12	-	_		_
19-21	-	-	•		_

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 10, 1975, at Pomona, California

NITROGEN COMPOUNDS

TIME (PDT)	CH ₂ CN fragment (relative)	CONH fragment (relative)	C _{3H5N2} fragment (relative)	CH ₂ NO ₃ fragment (relative)	C ₄ H _{8N2} fragment (relative)	C ₄ H ₉ N ₂ fragment (relative)	C ₅ H ₅ N Pyridine & Pyridyls	C ₅ H ₁₀ N Piperidines & Isomers
7-21	.20	2.0	-		_	.034	.0019	.0037
7-9	1.5	3.4	0	.32	0	-	.053	.14
9-11	.94	6.3	.03	_	.07	.11	.015	
11-13	.57	5.0	0	.10	-	• 1 1		.057
13-15	.12	1.4	_	.030	_	-	.012	.013
15-17	1.9	8.1	.10	.030	_	-	-	-
17-19	1.3	5.4	1.9	000	-	. 14	-	-
19-21	2.3			.090	-	-	-	-
19-61	2.3	3.0	. 7	-	~	-	-	

NITROGEN COMPOUNDS (cont.)

	_				(/	
TIME (PDT)	C ₇ H ₇ NO ₃ Hydroxynitro- toluene	C ₇ H ₇ NO ₄ Toluene oxidn. prod.	C ₉ H ₇ N Quinoline?	C _{lO} H ₇ NO ₂ Nitro- naphthalene	C ₁₂ H ₉ N Carbazole	C ₁₃ H ₉ N Acridine & Isomers
7-21	.0050	-	-	-		_
7-9	-	-	.034	· _	.011	_
9-11	-	-	.037	_	.0089	.016
11-13	-	-	-	-	_	_
13-15	-	_		-	_	_
15-17		-	.019	<u></u>	-	_
17-19	-	_	_	_	_	
19-21		.011	_	_	_	-
					_	_

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 10, 1975, at Pomona, California

	jd	INORGAN	NICS	CHLOR	INATED	COMPOUNI	OS
TIME (PDT)	Sulfates as Sulfuric Ac	Ammonium Chloride	Ammonium Nitrate	C ₁₂ H ₅ C1 ₃ PCB?	C7H4Cl ₃ Isodrin	C ₆ H ₄ Cl ₃ Lindane	C _S H _S Cl Heptachlor?
7-21	3.0	.40	>15	_	-	-	0
7-9	13.6	4.9	44	_	_	0	0
9-11	9.6	5.9	44	.084	.059	. 4	0
11-13	6.5	4.5	34	_	.084	. 12	0
13-15	2.3	.17	0.03	_	_	-	0
15-17	8.9	1.8	14	_		0	0
17-19	9.2	.37	_	_	_	O	U
19-21	2.7	-		-	_	. 35	0

TENTATIVE TERPENE PRODUCTS

TIME (PDT)	C ₉ H ₁₄ O ₂ Isomers	C ₁₀ H ₁₄ O ₃ Isomers	C ₁₀ H ₁₆ O ₂ Isomers	C _{lo} H _{l6} O ₃ Pinonic Acid?	C ₈ H ₁₂ O ₄ Norpinic Acid?	C ₉ H ₁ 40 ₄ Pinic Acid?
7-21	-	.058	-	_	_	
7-9	.13	-	_	. 14	_	_
9-11	.10	.27	-	_	-	_
11-13		_	-	-	_	-
13-15	.076	-	_	<u>.</u> .	_	-
15-17	.47	· <u>-</u>	-	_	_	-
17-19	.084	-	_	-	.11	-
19-21	-	-		_	- • T T	.12

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 10, 1975, at Riverside, California

ALIPHATIC HYDROCARBONS

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TIME (PDT)	C ₅ H ₁₁ Total Alkane	C ₆ H ₁₃ A1kane Low Mc	C ₆ H ₁₃ Alkane Med MW	C ₆ H ₁₃ Alkane High M	C ₅ H ₉ Total Alkenes	C ₆ H ₁₁ Alkenes Low MW	C ₆ H ₁₁ Alkenes Med MW	C ₆ H ₁₁ Alkenes High MW
7-21		0	.019		.18	_	.022	.088
7-9	.47	.09	. 14	.065	.90	.079	.22	.12
9-11		.035	.18	.09	.88	.047	.25	.29
11-13	.28	.08	.12	.033	.58	0	.12	
13-15	.12	.015	.078	.018	.62	.013	.19	.13
15-17	. 09	-	.10	.06	.37	.001	.084	.16
17-19	.17	-	.086	.002		-	.17	
19-21	.09	.040	.027	_	.29		.09	.09 .037
	7H ₇ ylenes, lkyl Benzenes	₈ H ₁₀ ylenes, thyl Benzenes	AROMATI	C HYDROCA		C ₁₃ H ₁₂ Diphenylmethane & Isomers		
TIME	հ, Iene Հy I	հ ₁₀ ene ւչյ1	C ₉ H ₁₁ Alkyl Benzene	C ₉ H ₁₂ Alkyl Benzenes	C ₁₀ H ₁₄ A1kyl Benzenes	12 eny ome		
(PDT)	C ₇ + Xy ₁ A1k	C ₈ H ₁ Xylei Ethy	С ₉ Н А1к Веп	C ₉ H A1k Ben	510 ¹ 41ky 3enz	iph iph Is		
7-21	.10	.009	.068	.022	040	.0020		
7-9	.38	.11	.035	.019	_	-		
9-11	. 37	.10	.144	.098	.035	_		
11-13	.19	.011	.049	~		_		
13-15	.19	.006	.033	.020	_			
15–17	.17	-	.047	_	_	_		
17-19	.20	.03	.030	.012	_	_		
19-21	.10	.006	.019	.0076	-			

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 10, 1975, at Riverside, California

		POL	YCYCLIC	AROMATI	CS		1	ene		
TIME (PDT)	С _в Н _в Tetrahydro-	naphthalene C9H10	C ₁₀ H ₉	Naphthalene C ₁₀ H ₁₈ Perhydro	naphthalene Cliffin	Mēthyl- naphthalenes	C ₁₁ H ₁₃ Dimethvltetra-	hydronaphthal C ₁₄ H ₁₀	Anthracene & Phenanthrene	C ₁₆ H ₁₀ Pyrene & Isomers
7 - 21	.033	.008	0 .00	69 .00	48 .C	020	.008		_	_
7-9	.19	.024	.016	5 -		_	_		_	_
9-11	.41	.021	.011	l -		~	.020) .	-	
11-13	.021	-	-	-		-	_	-	•	_
13-15	.057	-	.011	. –		-		_		_
15-17	.086	-	-	_		_	-	_		_
17-19	.041	.016	.004	_	,	-	.014	_		_
19-21	.016	-	0	_		-	-	_		_
				æ.						
		OXYG	SENATED	AROMATI	CS		+			
TIME (PDT)	C ₆ H ₄ O ₂ Benzoquinone?	C ₆ H ₅ O Phenol + NO ₂ ,CHO,COOH?	C ₆ H ₆ O Pheno I	C ₆ H ₆ O ₂ Dihydroxy- benzenes	C ₇ H ₆ O Benzaldehyde + Interference	C ₇ H ₈ O	Hydroxytoluene + Benzyl Alcohol	C ₉ H ₁₂ O Trimethylphenol + Isomers	C ₁₂ H ₁₀ O ₂ Biphenol	C ₁₄ H ₂₁ O Dibutyl- methylphenol
7-21	-	-	.010	.057			21	.019		
7-9	-	.31	.048	. 12	.023	.0		.061	-	_
9-11	-	.46	.09	.091	.039	.0		.026	-	~
11-13	-	.07	0	_		_	00	-	-	••
13-15	-	_	.053	.090	_	.03	37	.043	, -	-
15-17	-	-	0	.027	_	.05		.058		-
17-19	-		-	.041	0	.0.		- 056	-	-
19-21	-	.019	0	.053	_	.02		.011		-
						• 02		.011	-	.012

CONCENTRATIONS ($\mu g/m^3$)—OF AIR POLLUTANTS BY MSTA Sampled July 10, 1975, at Riverside, California

				010	CARBOXYL	IC ACIDS			U
TIME (PDT)	C ₂ H ₄ O ₂ Total Acids (as acetic)	C ₄ H ₆ O ₂ Pentanedioic Acid	C ₅ H ₈ O ₂ Hexanedioic Acid	C ₆ H ₁₀ O ₂ Methylhexanedioic Acid	С ₇ Н ₅ О Benzoyl Ion	C,H ₆ O ₂ Benzoic Acid	C ₈ H _{8O2} Methylbenzoic Isomers	C ₉ H ₁₀ O ₂ Ethylbenzoic Isomers	C ₁₀ H ₁₂ O ₂ Trimethylbenzoic Isomers
7-21	.31	.96	1.0	.47	.03	0	.012	.018	_
7-9	.77	1.2	5.1	.40	0	0	.043	.046	_
9-11.	.96	4.7	3.0	1.2	0	0	_	.092	_
11-13	.66	.75	-	-	0	0	_		_
13-15	.62	2.9	2.7	.81	.22	_	.027	_	_
15-17	.72	2.4	.73	. 15	.13		-	_	_
17-19	.38	1.3	.53	_	0	0	_	_	-
19-21	.27	.72	1.3	.67	.01	-	-	_	-

	ene	ene			SECO	NDARY DI	FUNCTIO	NALS	
TIME (PDT)	C ₅ H ₈ O ₃ Cyclohexene Product?	C ₅ H ₁₀ O ₂ Cyclohexe Product?	C ₅ H ₁₀ O ₃ Isomers	C ₆ H ₈ O ₂ 1-heptene product?	C ₆ H ₁₂ O ₃ Isomers	C ₇ H ₁₀ O ₂ Isomers	C ₇ H ₁₂ O ₂ Isomers	C ₇ H ₁₂ O ₃ Isomers	C ₈ H ₅ O ₃ Phthalates
7-21		-	.034	.41		.082	.023	.039	. 34
7-9	-	-	-	1.5	-	1.4	.37	_	2.1
9-11	.13	.16	.24	1.5	-	.60	.52	. 12	1.6
11-13	-	.17	-	~	•••	_	~	_	1.3
13-15	-		_	1.3	_	. 19		_	1.4
15-17	~	. -	_	.79	_	.48	.087	_	1.2
17-19	~	-	-	.75	_	-	. 10	_	.69
19-21	-	-	~	.46	-	.039	.071	_	1.2

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 10, 1975, at Riverside, California

SECONDARY DIFUNCTIONALS WITH NITROGEN

TIME (PDT)	С ₅ Н7NО ₄ НСО(СН ₂) ₃ СООNО	C ₅ H ₇ NO ₅ HOOC(CH ₂) ₃ COONO	C ₅ H ₇ NO ₆ Isomers	C ₅ H ₉ NO ₄ HCO(CH ₂) ₄ ONO ₂ + Isomers	C ₅ H ₉ NO ₅ HOOC(CH ₂) ₄ ONO ₂	C ₆ H ₉ NO ₄ HCO(CH ₂) ₄ COONO	С ₆ Н ₉ NО ₅ HOOC(СН ₂) ₄ COONO	C ₆ H ₉ NO ₆ Isomers
7-21	-	-	-	-	_	_	-	-
7-9	-		_	-	.28	_	_	_
9-11	-	_	_	.21	.31	_	_	
11-13	_	-	_	-		_	_	-
13-15	_	_	_	-	_		-	-
15-17	_		_	_	_	_	-	_
17- 19	_	~	_		-	-	-	
19-21	_		_	-	~	-	-	-
		-	-	-	.023	-	-	-

TIME (PDT)	C ₆ H ₁₁ NO ₄ HCO(CH ₂) ₅ ONO ₂ + Isomers	C ₆ H ₁ 1NO ₅ HOOC(CH ₂) ₅ ONO ₂	C ₇ H ₁ 1NO ₅ H0OC(CH ₂) ₅ COONO	C ₇ H ₁₃ NO _t HCO(CH ₂) ₆ ONO ₂ + Isomers	C ₂ H ₁₃ NO ₅ HOOC(CH ₂) ₆ ONO ₅ SECONDARY DIFUNCTIONALS + Isomers + Isomers +
7-21	.032	_	_	_	-
7-9	-	-	_	_	-
9-11	•••	-	_		-
11-13	-	-	-	-	-
13-15	.16	-	-	84	. -
15-17	~	_	_	-	· -
17- 19	-	-	_	***	_
19-21	· ~	-	-	-	_

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 10, 1975, at Riverside, California

NITROGEN COMPOUNDS

TIME (PDT)	CH ₂ CN fragment (relative)	CONH fragment (relative)	C ₃ H ₅ N ₂ fragment (relative)	CH ₂ NO ₃ fragment (relative)	C ₄ H _{8N2} fragment (relative)	C ₄ H ₉ N ₂ fragment (relative)	C ₅ H ₅ N Pyridine & Pyridyls	C ₅ H ₁₀ N Piperidines & Isomers
7-21	.26	1.5	0	-	0	.030	.00087	_
7-9	.19	5.1	-	.086	-	_	_	.041
9-11	.97	5.4	.01	-	_	_		
11-13	.17	4.1	_	_	_	_	-	.013
13-15	.88	4.1	_		.03	_	-	010
15-17	.20	2.1	.08	.067	.05	_	-	.012
17-19	-	2.7	0	_	-	_	_	•••
19-21	.088	1.3	.06	-	0	- -		- -

NITROGEN COMPOUNDS (cont.)

TIME (PDT)	C ₇ H ₇ NO ₃ Hydroxynitro- toluene	C ₇ H ₇ NO ₄ Toluene oxidn. prod.	C ₉ H ₇ N Quinoline?	C ₁₀ H ₇ NO ₂ Nitro- naphthalene	C ₁₂ H ₉ N Carbazole	C ₁₃ HgN Acridine & Isomers
7-21	-	-	.0073	_	.0018	••
7-9	-	-	.022	_	_	_
9-11	-	-	.037	_	.011	_
11-13	-	-	-		_	_
13-15	-	_	.011	_	_	_
15-17	-	_	.019		_	_
17-19	-	-	_	_	_	-
19-21	-	-	_	_	_	~
						-

CONCENTRATIONS ($\mu g/m^3$) OF AIR POLLUTANTS BY MSTA Sampled July 10, 1975, at Riverside, California

	70	INORGA	NICS	CHLO	CHLORINATED COMPOUNDS				
TIME (PDT)	Sulfates as Sulfuric Aci	Ammonium Chloride	Ammonium Nitrate	C ₁₂ H ₅ C1 ₃ PCB?	C ₇ H ₄ Cl ₃ Isodrin	C ₆ H ₄ Cl ₃ Lindane	C ₅ H ₅ Cl Heptachlor?		
7-21	3.5	0.08	4.3	.0097	A	-	0		
7-9	8.1	3.4	>50	-	-	0	0		
9-11	4.9	4.5	>40	_	_	0	0		
11-13	3.6	2.2	5.7	_		. 14	.17		
13-15	4.1	2.9	5.4	-	~	0	. 34		
15-17	2.8	.25	.45	_	.11	0	0		
17-19	2.3	. 18	.43	_	_	0	0		
19-21	1.8	~	0	-	-	0	-		

TENTATIVE TERPENE PRODUCTS

TIME (PDT)	C ₉ H ₁₄ O ₂ Isomers	C ₁₀ H ₁₄ O ₃ Isomers	C ₁₀ H ₁₆ O ₂ Isomers	C ₁₀ H ₁₆ O ₃ Pinonic Acid?
7-21	-	-	_	_
7-9	. –	-	_	_
9-11	-	.21	-	-
11-13	_	_	_	-
13-15	-	-	-	_
15-17	<u>-</u>	-	_	- ,
17-1 9	-	-	-	_
19-21	-	-		,

Appendix F

The Reactivity of Aerosol Components with Solvent Constituents

The extraction of aerosol constituents in refluxing polar methanol-chloroform for six hours provides ample opportunity for chemical reactions. For example, acids may form methyl esters with methanol, nitrates may hydrolyze to alcohols with the water likely to be present in the solvent or with water liberated by esterification reactions. If such reactions occur a number of errors may be introduced:

1. The number of carbons for individual compounds may increase.

€

- 2. Non-volatile compounds (e.g., dicarboxylic acids) may form relatively volatile products (e.g., di-esters) and be lost during the solvent removal procedure.
- 3. Determination of specific, reactive compounds by techniques such as MSTA would not be possible following extraction by the reactive solvent.

To evaluate the extent of such errors an experiment was performed with realistic concentrations of known carboxylic acids under simulated extraction conditions. Two acids were used, hexanedioic (adipic) and abietic acid, a mono-carboxylic acid ($C_{20}H_{30}O_{2}$) found in rosin. 0.4 mg of each compound was refluxed for six hours in ca. 60 ml 2:1 v/v chloroform-methanol. In an additional experiment, 0.4 mg of hexanedioic acid was added to a concentrated chloroform-methanol extract of a 14-hour atmospheric filter sample, the solution diluted to about 60 ml with the solvent and refluxed six hours. The solutions were reduced in volume to 10 ml and, except for the spiked extract, aliquots evaporated to dryness for carbon analysis as detailed in Appendix C. The latter includes vacuum treatment for 30 minutes at room temperature.

The carbon analysis results for hexanedioic acid indicated 38% recovery (mean of three determinations) relative to the initial carbon due to the acid. In contrast the results with abietic acid indicated a mean recovery of 103%.

In an effort to follow any chemical changes occurring, infra-red spectra were determined with a Perkin-Elmer 62l grating spectrometer for fresh and refluxed reactants. Because of the low concentrations involved and because of spectral interference from the solvent, spectra were only obtainable by evaporating ca. 50% of the total extracts onto salts plates. The resulting spectra exhibited weak carbonyl bands which were notably shifted from that expected for carboxylic acids. The IR results are summarized in Table F-1. Hexanedioic acid gave evidence of ester formation with the corresponding carbonyl band substantially more intense than that ascribed to the acid. With abietic acid, ester formation as evidenced by carbonyl changes, occurred to a much lesser degree. The small differences between observed and expected carbonyl positions are ascribed to the absence of solvent in the present spectra.

The loss of hexanedioic acid during carbon determination can be ascribed to volatization of the di-ester (molecular weight 174.2) which is a liquid at room temperature, boiling point 115°C (at 13 mm Hg). The apparent high recovery of abietic acid during carbon determination may be ascribed to its lesser degree of ester formation and to the relatively low volatility of its methyl ester (molecular weight 332, boiling point 225°C at 16 mm Hg).

The significance of these findings to MSTA results is apparent; it is expected that carboxylic acids and other reactive organics (e.g. acid nitrates) not previously extracted in benzene would be largely reacted in the mixed solvent and, therefore, undetectable by MSTA. The significance of these findings for carbon determinations is more subtle since it depends on the volatility of any reaction products. Control experiments described in Table D-4 of Appendix D indicate for an MCC sample loss of only 4% carbon during the 30-minute vacuum treatment. Since, prior to the vacuum treatment, solvent was removed at about room temperature into a moving stream of particle-free air we assume (but cannot prove) that the 4% loss of carbon reflects the loss of particulate organics for the entire solvent removal process.

If it is accepted that the organics recovered from the methanol-chloroform extract are relatively non-volatile than a positive error should be introduced in the carbon determinations due to the addition of carbon from the solvent in forming products such as esters and ethers. The significance of this error depends on the average number of carbons in the particulate organics and the fraction of the carbon atoms bearing reactive groups available for ester or ether formation. If the average number of carbons in the MCC fraction is assumed to be six and 10% of all carbons assumed able to react with addition of CH₃O-from methanol, then a 10% positive error in carbon determination would be introduced.

While techniques such as nuclear magnetic resonence could be useful in directly monitoring such solvent-particulate reactions by measuring changes in CH_3 or CH_3O content, this was not currently feasible.

Table F-1

INFRA-RED SPECTRAL RESULTS FROM REACTION OF

CARBOXYLIC ACIDS WITH CHLOROFORM-METHANOL^a

<u>Sample</u>	Carbonyl Peak Positions, (cm ⁻¹)	Expected Carbonyl. Positions, (cm ⁻¹)
Hexanedioic acid, unreacted	1680	1700
Hexanedioic acid, refluxed in chloroform-methanol	1720 (weak) 1690 (shoulder)	
Methylester of hexanedioic acid	· · · · ·	1739
Abietic acid, unreacted	1700-1710 (weak, broad)	1705-1725
Abietic acid, refluxed in chloroform-methanol	1735 (weak) 1700 (weak)	
Methylester of abietic acid		1735-1750
Hexanedioic acid, refluxed in chloroform-methanol with atmospheric extract	1710-1725 (weak, broad) 1690 (shoulder)	
Hexanedioic acid, unreacted in chloroform-methanol with atmospheric extract	1680 (shoulder)	1700

a. All spectra obtained on samples evaporated onto a NaCl plate from methanol-chloroform solution.

b. L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," Wiley and Sons, New York (1958).

Appendix G

The solvent extraction-carbon analysis data were compiled and keypunched according to the format given in Table G-1. The data are included as Table G-2.

Table G-1

FORMAT FOR SOLVENT EXTRACTION-CARBON ANALYSIS DATA

Column	<u>Use</u>
1-8	Filter code: wx yyyy zz
	where w = station code, C = Pasadena P = Pomona R = Riverside
	x = Episode designation by day, A,B,C
	yyyy = Filter number
	zz = Filter type, HR indicates glass fiber filter
10-15	Date sampled
17-25	Time of Day (PDT)
28	Analytical lab. A indicates AIHL
29-34	Date analyzed
35-37	Species analyzed: CEL = total carbon MCC = methanol-chloroform extractable carbon BEC = benzene extractable carbon CEC = cyclohexane extractable carbon
39-43	Flow rate, m^3/cm^2
45-53	Concentration, $\mu g/m^3$
55-63	Analytical error, $\mu g/m^3$
68-69	Filter section number. L and R indicate left and right filter halves (arbitrary designation).
74-76	Hi-vol sampler number.

Table G-2

Solvent Extraction-Carbon Analysis Data

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Appendix H

Glossary of Terms and Abbreviations

ACHEX - Aerosol Characterization Experiment

BEC - benzene extractable carbon

b_{scat} - light scattering coefficient

Cp - primary organic carbon

Cs - secondary organic carbon

Ce - elementary organic carbon

CEC - cyclohexane extractable carbon

CEL - total carbon (all forms)

GC-MS - gas chromatography - mass spectroscopy

MCC - methanol-chloroform extractable carbon

MSTA - mass spectrometric thermal analysis

PDT - pacific daylight time

PNA - polynuclear aromatic

TSP - total suspended particulate matter